Preparation of Interconnected Biomimetic Poly(vinylidene fluoride-co-chlorotrifluoroethylene) Hydrophobic Membrane by Tuning the Two-Stage Phase Inversion Process

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Supporting Information

ABSTRACT: A facile strategy was applied for poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) hydrophobic membrane preparation by tuning the two-stage phase inversion process. The exposure stage was found to benefit the solid–liquid demixing process (gelation/crystallization) induced by the solvent evaporation and the subsequent phase inversion induced by immersion benefit the liquid–liquid demixing. It was confirmed that the electrospun nanostructure-like biomimetic surface and interconnected pore structure can be expected by controlling the exposure duration, and 300 s was considered as the inflection point of exposure duration for PVDF-CTFE membrane through which a tremendous variation would show. The micro/nanohierarchical structure in the membrane surface owing to the crystallization of PVDF-CTFE copolymer was responsible for the improvement of membrane roughness and hydrophobicity. Meanwhile, the interconnected pore structure in both the surface and the cross-section, which were formed because of the crystallization process, offers more mass transfer passages and enhances the permeate flux. The membrane then showed excellent MD performance with high permeate flux, high salt rejection, and relatively high stability during a 48 h continuous DCMO operation, according to the morphology, pore structure, and properties, which can be a substitute for hydrophobic membrane application.

KEYWORDS: biomimetic membrane, interconnectivity, crystallization, two-stage phase inversion, exposure duration

INTRODUCTION

Membrane distillation (MD) is a promising membrane process in seawater desalination, water purification, and resource recovery processes which have been widely studied since the 1960s.¹ It is a thermal-driven process, in which the membrane guarantees that only vapor/gas can transfer through the membrane.^{2,3} Thus, it can offer high separation efficiency especially in desalination application (theoretically 100%). MD combined the traditional distillation and the membrane process, which enjoy numerous benefits in water treatment and desalination due to the low-energy requirement, low cost, and low-operational pressure.^{2,4,5} However, hydrophobic membranes with desirable structure and properties were the biggest obstacle for MD application because of the membrane wetting and fouling issues, low water productivity, and short lifespan, especially when speaking to MD industrial extension.^{6–10}

Inspired by the natural hydrophobic/superhydrophobic surface like lotus leaves, gecko feet, and rose petals, the preparation of hydrophobic membranes with a biomimetic surface has become a growing research topic in recent years.^{11–13} The hydrophobicity/superhydrophobicity surface is characterized by papillose and microgrooved structure with high roughness, where the microhierarchal and nanohierarchal morphologies offer a higher contact angle (CA) because of the air trapped in the “pockets” according to the Cassie–Baxter equation.^{12,14} Thus, tailoring the membrane interfacial morphology and surface pore structure with micro/nanobump structure aiming to control the surface wettability has been widely investigated. Li et al.⁹ prepared dual-

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biomimetic hierarchically polystyrene (PS) micro/nanofibrous membrane by electrospinning. The membrane exhibited a nanopillose, nanoporous, and microgrooved surface like lotus leaf, so it was superhydrophobic and presents excellent MD desalination performance (permeate flux of 104 kg/m²·h as ΔT was 50 °C). Hydrophobic nanoparticles have also been applied for hydrophobic composite membranes preparation; the resultant membranes showed higher porosity and superhydrophobicity due to the microstructure formed by the doped nanoparticles. Thus, the membrane has excellent waterproofing property and breathability especially when electrospinning was applied.^{8,15–19} Photoinitiated polymerization-induced phase inversion was also used to generate a rough surface like rose petals in the membrane surface, and the resultant membrane showed parahydrophobicity with a high contact angle.¹¹ To date, a diversified strategy like electrospinning, addition of hydrophobic nanoparticles, surface coating or cross-linking, and chemical vapor deposition was applied for biomimetic membrane preparation, tuning the surface with micro/nanohierarchical structure and an interconnected surface pore structure were the basic principles.^{6,13,20–27}

The surface pore structure also significantly influences the membrane selectivity. The pore structure with high interconnectivity guarantees high rejection with desired flux and vice versa. Meanwhile, the pores in cross-section, which act as the effective mass transfer passages, guarantee the membrane permeability as the pores were highly interconnected. Thus, the interconnectivity should be highlighted when evaluating the permeability of membranes. In recent years, preparation of membranes with interconnected pore structure has been another direction in membrane science.^{27–29} Recently, electrospinning technology has been used to fabricate hydrophobic membranes. The membranes prepared by electrospinning present interconnected pore structure due to the layer-by-layer accumulation of nanofibers and higher roughness because of the nanoarched structure in membrane surface, which has ideal structure and properties for MD applications and has shown excellent performance on MD process.^{6,30} However, the slow membrane formation rate, high voltage operation condition, and high investment confined its commercial applications. Phase inversion, a traditional membrane preparation technology, finds most applications especially in commercial process.

Four phase inversion processes including thermally-induced phase inversion (TIPS), vapor-induced phase inversion (VIPS), nonsolvent diffusion-induced phase inversion (DIPS) (also known as the immersion phase inversion), and evaporation-induced phase inversion (EIPS, also known as air casting) were commonly applied for polymeric membrane preparation.^{31,32} The solution was immersed in a nonsolvent coagulation bath after casting, and the immediate phase inversion was induced by the fast exchange of solvent and nonsolvent in the DIPS process. In the VIPS process, the nonsolvent vapor (commonly water) permeates to the casting solution induced the delayed phase inversion process. While the phase inversion can be induced by solvent evaporation or water vapor adsorption by solvent, the solid–liquid process happened in both processes and the phase inversion rate was slow in the EIPS process. Generally, membrane prepared by VIPS or EIPS showed particulate-packed interconnected structure due to the solid–liquid demixing (S–L demixing) by polymer gelation or crystallization, while membrane prepared by DIPS showed

typical asymmetric structure including a dense top layer, macrovoids layer, and sponge-like sublayer due to the instantaneous liquid–liquid demixing (L–L demixing).^{33,34} Controlling the gelation/crystallization of polymer by tuning membrane preparation condition or adding extra additives to acquire interconnected pore structure and hydrophobic surface has been widely investigated in hydrophobic membrane preparation. A two-stage phase inversion strategy by two coagulation baths with at least one soft nonsolvent (nonsolvent which has low interaction with solvent such as ethanol) has been applied for polymeric membrane preparation, through which the membrane morphology and pore structure were tuned by controlling the phase inversion rate.^{35,36}

In this contribution, a two-stage phase inversion strategy combining EIPS and DIPS was applied to prepare poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) membrane, and the biomimetic membrane was prepared by the facile NIPS method for the first time by controlling the duration of two stages. The effect of the evaporation duration on membrane morphology, properties, and MD performance was investigated. Specifically, the effect of the first stage phase inversion induced by solvent evaporation on the subsequent phase inversion in coagulation bath was carefully characterized and analyzed to understand the membrane formation process. Membrane surface pore structure was carefully studied in terms of morphology, pore structure, roughness, and hydrophobicity to obtain a complete understanding of the phase inversion process during membrane formation by field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and SEM image analysis. The overall pore structure and MD performance were also studied to evaluate the resultant membranes. In particular, the pore interconnectivity was highlighted as an important factor for membrane evaluation because it was highly related to the mass transfer in the membrane process. Clearly evidence showed that the exposure duration has a significant influence on the resultant membranes. An inflection point, an exposure time through which the radical change would appear, was clearly observed and confirmed by all characterizations. It was sure that the interconnected biomimetic membrane can be obtained by tuning the two-stage phase inversion process, and the PVDF-CTFE membrane showed great potential for MD application.

EXPERIMENTAL SECTION

Materials. PVDF-CTFE (Solef 32008 with $M_w = 280\,000$, VF₂:CTFE = 80:20, Solvay, Belgium) was desiccated at 50 °C for moisture removal. Dimethyl acetamide (DMAc, >99%) was obtained from Shanghai Jingwei Chemical Co., Ltd. (Shanghai, China). LiCl and polyethylene glycol (PEG) mixture at a mass ratio of 1:1 was used as the additives; both LiCl (AR, >95%) and PEG-400 (AR, >99.5%) were supplied by the Tianjin Guangfu Research Institute of Fine Chemical Engineering (Tianjin, China). Ethanol (GR grade, 99.9%) and NaCl (GR grade, 99.5%) were purchased from Beijing Chemical works (Beijing, China). Tap water was used as coagulant. All reagents were used as received except the PVDF-CTFE powder.

Membrane Preparation. PEG-400 (4 g) and LiCl (4 g) were mixed with DMAc (80 g) in a sealed flask and stirred at 30 °C until all additives are completely dissolved. Then 12 g of predesiccated PVDF-CTFE powder was added to the flask, and the mixture was continuously stirred for at least 24 h to obtain a homogeneous solution. Then the polymer solution was kept in a vacuum oven for at least 24 h for vacuum degassing at 30 °C.

Hydrophilic polyethylene terephthalate (PET) nonwoven fabric was used as the supporting material to prevent membrane shrinking and to enhance the mechanical strength, which was attached to a clean flat

glass at the beginning. The degassed homogeneous casting solution was uniformly spread on the nonwoven fabric with a knife gap of 0.25 mm at 50 °C. After being exposed in the oven for a predesigned time, the cast film was immersed into a 25 °C water bath. Twenty-four hours later, the membrane was fetched out from the coagulation bath and rinsed with tap water to further remove the residual solvent and nonsolvent additives. Last, the wet membrane was air dried at room temperature. Nine membranes were prepared at different exposure durations to study the effect of exposure duration on PVDF-CTFE membranes (detailed membrane preparation conditions are listed in Table 1).

Table 1. Preparation Conditions of PVDF-CTFE Membranes

membrane code	exposure temperature and time (°C, s)	coagulation temp. (°C)
M1	50, 0	25
M2	50, 5	25
M3	50, 10	25
M4	50, 30	25
M5	50, 60	25
M6	50, 180	25
M7	50, 300	25
M8	50, 600	25
M9	50, 1800	25

Morphology. Field emission scanning electron microscopy (FE-SEM, HITACHI SU8020, Hitachi, Japan) was used for membrane morphology observation. The membranes were cryogenically fractured in liquid nitrogen for observation of the membrane cross-section. Before SEM observation, all samples were coated with gold nanoparticles under vacuum conditions by an ion sputtering device (HITACHI E-1010, Hitachi, Japan). An atomic force microscope (AFM, Shimadzu SPM-9600, Shimadzu, Japan) was employed to analyze the surface morphology and roughness of the flat-sheet membranes. All membranes were measured by tapping mode with the same probe at a scan size of 5.0 $\mu\text{m} \times 5.0 \mu\text{m}$. The 3D surface morphology and depth distribution images were obtained as well as the mean surface roughness R_a , the root-mean-square of the Z data R_q , and the mean difference between the five highest peaks and lowest valleys R_z .

Thermal and Crystalline Properties. The infrared spectrum of the membranes was evaluated using a Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA). All spectra were recorded in a wavenumber range of 1600–650 cm^{-1} by cumulating 64 scans at a resolution of 4 cm^{-1} . According to the spectrum, the content of β phase F_β was

calculated by the following equation which has been widely applied^{37–39}

$$F_\beta = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \quad (1)$$

where A_α and A_β represent the absorbency at 766 (α phase) and 840 cm^{-1} (β phase) and K_α and K_β are the absorption coefficients at the respective wavenumber, the values of which are 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2/\text{mol}$, respectively.

Differential scanning calorimetry (DSC) was used to determine the thermal properties (melting temperature T_m and crystallinity) of the membranes by a DSC 2 STAR[®] system (Mettler Toledo, Switzerland). About 5 mg of membrane coupons was torn off from the supporting layer and placed in a 40 μL aluminum crucible. Then the crucible was placed in the instrument and heated from 80 to 250 °C at a rate of 10 °C/min. The heat flow was recorded, and then the crystallinity χ was calculated by the following equation⁴⁰

$$\chi = \frac{\Delta H_m}{x(\Delta H_{100\% \text{cryst}})_\alpha + y(\Delta H_{100\% \text{cryst}})_\beta} \quad (2)$$

where x and y are the fraction of α phase and β phase, ΔH_m is the recorded melting enthalpy of the membrane, and $(\Delta H_{100\% \text{cryst}})_\alpha$ and $(\Delta H_{100\% \text{cryst}})_\beta$ represent the melting enthalpy of the pure α -PVDF and β -PVDF crystalline which are reported to be 93.04 and 103.4 J/g, respectively.⁴¹

Hydrophobicity. The hydrophobicity of the membrane was characterized by static water contact angles (CA_w). The CA_w of membranes were measured by an OCA 15EC Video-Based Contact Angle Meter (Data Physics, Germany); 5 positions were measured for each membrane.

Pore Structure. Membrane surface pore structure was analyzed according to the SEM micrographs; the pores in the membrane surface were marked in blue as shown in Figure S4 by the image-pro-plus 6.0 software (Media Cybernetics, USA). The minimum, maximum, and average pore sizes were recorded to represent the pore size in the membrane surface as well as the pore distribution. Surface porosity and the mean roundness of surface pores were also calculated to indicate the pore surface structure. The detailed method can be found in the Supporting Information.

The overall pore size and pore size distribution of the prepared membranes were investigated using a Capillary Flow Porometer Porolux 1000 (Porolux, Belgium) by the capillary flow method⁴² (detailed description can be found in the Supporting Information). The overall porosity ε defined as the ratio of the volume of the overall pores and the total volume of the PVDF-CTFE layer was determined by the gravimetric method and calculated by the following equation

Figure 1. FTIR spectra (A) and DSC traces (B) of the PVDF-CTFE membranes.

Table 2. Thermal, Crystallinity, Roughness, Hydrophobicity, and β -Phase Content of PVDF-CTFE Membranes

membrane code	β -phase content (%)	T_m (°C)	crystallinity (%)	Ra (nm)	SEM roughness index	CA_{water} (deg)
M1	87.50	164.67 $\pm$ 0.35	24.28	22.95	28.16	82.92 $\pm$ 2.0
M2	92.63	164.83 $\pm$ 1.13	24.50	29.39	29.13	82.30 $\pm$ 1.6
M3	90.36	167.33 $\pm$ 0.57	28.20	27.89	28.05	85.42 $\pm$ 5.9
M4	94.37	166.83 $\pm$ 0.83	30.19	32.74	29.39	85.50 $\pm$ 0.7
M5	92.69	166.00 $\pm$ 1.25	30.22	40.87	32.83	90.37 $\pm$ 4.0
M6	85.94	165.67 $\pm$ 0.54	30.52	40.30	33.89	97.74 $\pm$ 1.8
M7	80.13	166.67 $\pm$ 0.76	39.13	68.44	49.97	98.18 $\pm$ 3.3
M8	77.29	168.00 $\pm$ 0.18	38.59	146.60	43.11	102.38 $\pm$ 1.2
M9	73.06	167.50 $\pm$ 1.04	39.33	112.12	36.32	105.23 $\pm$ 1.1

Figure 2. Membrane surface morphology by FE-SEM (M1–M6, 50 000 magnified image inset in 5000 magnified image; M7–M9, 5000 magnified image inset in 1000 magnified image).

$$\varepsilon = \frac{(M_w - M_d)/\rho_w}{(M_w - M_d)/\rho_w + M_d/\rho_p} \quad (3)$$

where M_w is the weight of the wet membrane, M_d is the weight of the dry membrane, and ρ_w and ρ_p are the density of water and polymer powder, respectively. The detailed measurement method can be found in the [Supporting Information](#).

Direct Contact Membrane Distillation (DCMD). A lab-scale DCMD setup as shown in [Figure S1](#) was applied to study membrane permeability and sustainability (detailed conditions of the setup can be found in the [Supporting Information](#)). Feed solution (35 g/L aqueous NaCl solution) flowed on the upper layer of PVDF-CTFE membrane, and distilled water was circulated on the surface of PET supporting layer; the flow rate of feed and permeate was kept constant at 65 and 50 L/h. Convection current was applied to prevent the accumulation of gas bubbles in the module which may influence the effective area of the membrane. The temperature on the inlet of the distillate and the feed solution was kept at 25 and 55 °C, respectively.

RESULTS AND DISCUSSION

Membrane IR Spectrum and Thermal Properties.

[Figure 1A](#) presents the Fourier transform infrared spectroscopy (FTIR) spectrum of the membranes; specific adsorption bands of 840, 862, 1073, 1173, 1276, and 1430 cm^{-1} could be observed. That means both α - and β -phase existed in the

resultant membranes, as 763 and 862 cm^{-1} were the adsorption bands of α -phase and 840 and 862 cm^{-1} indicate the presence of β -phase.^{37,40} Meanwhile, the polymorphs showed no variation as the exposure duration increased because no obvious variation can be found in the position of the characteristic peaks. However, the β -phase content varied as can be found in [Table 2](#); it was about 90% for membranes M1–M5, indicating that the β -phase was the dominant polymorph in all PVDF-CTFE membranes, while it decreased as the exposure duration was higher than 180 s, which may result from the polymer crystallization process and the aggregate of the crystals in membrane which will be discussed in the SEM micrographs in [Figure 2](#).

The thermal properties were also investigated; the DSC curves are presented in [Figure 1B](#). All membranes exhibit almost similar melting temperatures (T_m) between 164 and 168 °C, consistent with the T_m of α -phase and β -phase.^{39,41} However, the T_m slightly increased with increasing exposure duration because of the increase of α -phase content. Meanwhile, it was clear that the crystallinity increased when increasing the exposure duration, especially when the exposure time was higher than 300 s as shown in [Table 2](#). The increase of the α -phase may be one reason, while the phase inversion during exposure stage was another reason. During the air

Figure 3. Three-dimension morphology of the membrane surface by AFM .

exposure stage in the oven at 50 °C, the solvent evaporated after solution casting, so the polymer-rich phase would be formed and the gelation or crystallization process would be induced especially for the upper layer. When enhancing the air exposure stage, the solvent evaporation-induced phase inversion has more time to proceed and the gelation/crystallization would process more thoroughly. As a result, the crystallinity of the membrane increased. Thus, it can be inferred that the phase inversion process by different exposure times would have a significant influence on the membrane morphology and properties.

Surface Morphology and Properties. Membrane skin layer was the function layer in the membrane process, so the morphology, especially the pore structure of the membrane surface, has a tremendous influence on the membrane separation performance. Meanwhile, the skin layer also influenced the subsequent phase inversion process of sublayers during membrane formation, which then influence the final membrane structure and performance.⁴³

Figure 2 shows the SEM micrographs of the resultant membranes; M1–M6 are presented with 50 000× magnified image inset in the 5000× magnified image; however, the 5000× magnified image was inset into the 1000× magnified image for M7–M9 because of the higher pore size. All membranes showed open porous structure with crystals in the surface, which presented a similar microstructure as the lotus leaf (for M1–M6) and the electrospun nanofiber membrane (for M7–M9), because PVDF-CTFE has a higher crystallization tendency as confirmed in our previous work.⁴⁴ The crystals and particles aggregate pore structure became more significant as the exposure duration increased especially as can be found in the inserted images in Figure 2. The membrane 3-D surface morphology and membrane surface depth distribution image recorded by AFM are presented in Figure 3 and Figure S2, respectively. The biomimetic micro/nano-hierarchical structure was confirmed by Figure 3 as the polymer nodules can be found in the membrane surface. As a result, the roughness and crystals size increased along with the increasing exposure duration so as the water contact angle as shown in Table 2. Meanwhile, the roughness and hydrophobicity also presented a significant increasing trend as the exposure time was higher than 300 s

(Table 2 and Table S1). The contact angle of all membranes was higher than 82°, so the PVDF-CTFE membranes were believed to be suitable in the MD process, while for M7, M8, and M9, the contact angles were 98.18°, 102.38°, and 105.23°, respectively. The hydrophobicity was higher as compared to the original PVDF membranes without hydrophobic modification, which usually has a contact angle between 65° and 80°.

The phase inversion process in the exposure stage was believed to be the main reason for membrane surface morphology variation. The solvent evaporated, and the gelation/crystallization process happened first on the air–solution interface as the solution had been casted. Thus, the polymer concentration became higher and the crystallization line was crossed; then the crystals were formed in the membrane surface, and papillose biomimetic structure can be found. For the membranes prepared by a shorter exposure stage, the L–L demixing would immediately be induced as the cast film was immersed into a coagulation bath, even the S–L demixing still proceeded in coagulation, so the net-like pores in membrane surface were formed as a result. When further increasing the exposure duration, more time was available for S–L demixing and the crystals would aggregate together. It can be attributed to explain the open porous structure and nanofiber-like structure as shown in membranes M7–M9. This evidence clearly showed that the S–L demixing had a more significant influence when increasing the exposure duration, resulting from the higher concentration of polymer due to solvent evaporation and sufficient time for the gelation/crystallization process. Thus, we can surely infer that the final morphology of the membrane surface was affected by the two-stage phase inversion process as the exposure duration was lower than 180 s. However, when the exposure duration was higher than 300 s, which can be viewed as an inflection point as also confirmed by the data of crystallinity, the nodules aggregation became more significant and the structure was similar to the membrane prepared by electrospinning.^{8,45} This indicates the phase inversion of the surface layer was almost complete after 300 s in air. Also, it is may be the reason why the inflection point can be observed.

The variation of surface roughness and hydrophobicity was also believed to be in consequence with polymer crystallization

Table 3. Membrane Pore Structure in Terms of Pore Size, Porosity, and Roundness

membrane code	surface pore structure			overall pore structure		
	pore size ^a (μm)	porosity (%)	roundness	pore size ^b (μm)	pore size ^a (μm)	porosity (%)
M1	0.1024	20.29	1.85	0.5097 ± 0.073	0.1130 ± 0.040	60.37 ± 3.8
M2	0.1217	24.37	2.10	0.2310 ± 0.065	0.1313 ± 0.035	61.00 ± 0.4
M3	0.1266	27.16	1.86	0.2255 ± 0.038	0.1436 ± 0.021	61.08 ± 2.4
M4	0.1140	24.04	1.79	0.3043 ± 0.046	0.1819 ± 0.067	64.26 ± 3.7
M5	0.1062	19.69	1.66	0.3685 ± 0.068	0.1788 ± 0.043	63.69 ± 0.4
M6	0.1194	26.20	2.08	0.5325 ± 0.105	0.1960 ± 0.094	71.93 ± 2.3
M7	0.3616	46.97	2.35	1.205 ± 0.138	0.2971 ± 0.085	54.68 ± 3.4
M8	0.4189	51.43	2.12	1.704 ± 0.317	0.6521 ± 0.143	50.98 ± 1.1
M9	0.3523	40.26	2.03	2.323 ± 0.419	0.9297 ± 0.186	50.84 ± 1.0

^aMean pore size. ^bBubble point pore size.

during the phase inversion process. As the crystals formed more completely when the exposure duration was longer and aggregate together after the inflection point was passed, the surface roughness would increase as verified by both AFM and SEM image analysis (showed in Table 2 and Table S2) because of the presence of the crystals and crystalline nodules. The crystals and crystalline nodules in the membrane surface can also be used to explain the increase of contact angle, as the membrane hydrophobicity was highly consistent with the roughness in hydrophobic materials.⁴⁴ On the basis of these considerations, the inflection point also had an effect on membrane roughness and hydrophobicity.

Membrane Surface Pore Structure. As can be found from the SEM micrographs displayed in Figure 2, the membrane surface pore structure was significantly influenced by the exposure stage. By further analysis of the 10 000× magnified SEM micrographs (the original image can be found in Figure S4), detailed surface pore structure information was obtained and is listed in Table 3 and Table S2. A clear consistency can be found between the surface pore size and porosity; both increased in the beginning, then decreased, and finally significantly increased as the exposure duration was higher than 300 s. A gel layer would first form due to the polymer gelation/crystallization happening in air because of solvent evaporation.^{46,47} Thus, the S–L demixing would have a more significant role on the phase inversion process as exposure duration increased. When exposure time was shorter than 30 s, the polymer-rich phase and polymer-lean phase separated more completely and benefit the pore formation process after being immersed in the coagulation bath as the exposure stage increased. As more exposure duration offered, the gel layer would in turn delay the phase inversion process in coagulation as the polymer concentration in the surface layer was higher due to evaporation of solvent.⁴⁷ However, when the inflection point was surpassed, complete phase inversion was achieved for the surface layer and the crystals formed by solidification in air would aggregate and even formed electrospinning nofiber-like structure as shown in Figure 2. Thus, the pore size and porosity in the membrane surface would increase again due to the high exchange rate of solvent and nonsolvent after immersion. It also worth noting that the roundness of the pores presents a highly relevant trend with pore size, which is also strongly related to the polymer solidification process.

The surface pore distribution was also obtained by SEM image analysis as shown in Figure 4. The pore size increased, decreased, and reincreased with increasing exposure time as Table 3 shows. It was also interesting to find that the surface

Figure 4. Pore size distribution of membrane surface pores.

pore distribution remained narrow and centralized for membranes M1–M6 as exposure duration was lower than 180 s, which became much broader and decentralized when the inflection point was surpassed. The crystal aggregation was believed to be the main reason for the variation in the pore distribution, which was also consistent with the membrane surface morphology and pore size. In other words, the variation in the pore structure was also significantly influenced by the phase inversion process in the air exposure stage and immersing stage.

Membrane Cross-Section Structure. The SEM images of the membranes cross-section are presented in Figure S5 to illustrate the effect of the exposure stage on the morphology and pore structure of the membrane cross-section. All membranes showed asymmetric structure constituted by a top layer, macrovoids, and sponge-like sublayer typically formed by L–L demixing when the exposure duration was lower than 180 s. However, the pore interconnectivity increased in both the macrovoids and the sublayer (sponge-like layer) as the exposure time increased. Distinguishingly, when the exposure time was higher than 300 s, i.e., the inflection point, the membranes presented symmetric structure with polymer crystals. Two stages of macrovoids suppression can also be found, which was also reported for PSf hollow fiber membranes,⁴⁶ and the phase inversion process that happened in the exposure stage was believed to be the reason in that work. To further study the phase inversion process during the air exposure stage and the coagulation stage, especially their interactive effects on the resultant membranes, the upper layer

Figure 5. Morphology of the upper layers of the membrane cross-section.

Figure 6. Pore size distribution of membrane overall pores.

near the top layer was carefully observed by FE-SEM. It can be found in Figure 5 that the membrane top layer (1) became thinner and more porous as the exposure duration extended; it even disappeared when the time was higher than 300 s. The macrovoids layer (2) also presented the same trend as the top layer with interconnected and particulate pore structure. As for the sublayer (4), Figure 5 clearly shows that the interconnectivity increased with increasing exposure duration.

The two-stage phase inversion processes during the air exposure and coagulation stage were responsible for the final cross-section morphology and the pore structure. As the two-stage phase inversion strategy was applied, the crystallization/gelation in the air exposure stage and rapid L–L demixing in the coagulation bath worked together to influence the final membrane. Meanwhile, the S–L demixing still goes on when cast film was immersed in the coagulation bath. As we know, the membrane formed by S–L demixing and L–L demixing has a different morphology and structure. The L–L demixing

dominates the phase inversion process when the exposure stage was short (lower than 180 s), because the L–L demixing happened immediately after immersion. However, the S–L demixing showed more influence when increasing the exposure duration. One reason is that the time for solvent evaporation in air was longer which induced more complete crystallization. The other reason is that the exchange of solvent and nonsolvent was impeded because of the gel layer in the membrane surface formed in air, so more time was available for S–L demixing in the coagulation bath, which then resulted in the interconnected particulate structure, and the macrovoids were also suppressed because of the existence of the top layer. That also explained the higher pore interconnectivity, bigger nodules, and more symmetric structure of the cross-section. When the exposure time was higher than 300 s, the formation of the membrane surface layer was almost complete, the S–L demixing dominates the phase inversion process, and the symmetric membrane was obtained. However, the membrane

Figure 7. Membrane permeate flux and conductivity in DCMD desalination process (feed temperature, 55 °C; permeate temperature, 25 °C).

Figure 8. Permeate flux and conductivity of PVDF-CTFE membrane during a 48 h continuous MD operation (feed temperature, 55 °C; permeate temperature, 25 °C).

interconnectivity decreased as the exposure time was higher than 300 s because of the aggregation of crystals due to the S–L demixing process before immersion. The particles in the surface even aggregate to form a bigger crystalline structure or nanofiber-like structure. In other words, the membrane prepared by exposure times higher than 300 s can be considered to be prepared by a solvent evaporation-induced phase inversion as the solidification process was almost finished in the exposure stage, especially for the upper layers.

Membranes Overall Pore Structure. The surface pore structure significantly influences the rejection performance (or separation factor) in the membrane process, while the overall pore structure would highly relate to membrane permeability. Pore size including bubble point, minimum, mean pore size, and the overall porosity were measured here to study the effect of exposure duration on the membrane overall pore structure, and the results are shown in Table 3 and Table S2. It can be found that the membrane pore size and overall porosity increased along with the exposure duration, and an inflection point at 300 s can also be observed. The competition of S–L demixing and L–L demixing during the two-stage phase

inversion process was believed to be the main reason. The pore size distribution of the membranes is presented in Figure 6. A narrow and centralized pore distribution was obtained when exposure time was less than 180 s, and it became remarkably broader and decentralized when exposure duration was longer than 300 s as the crystals aggregated together, which was in accordance with the pore size data shown in Table 3.

Membrane Distillation Performance. As it was surely believed that the phase inversion in the exposure stage had a significant influence on PVDF-CTFE membrane morphology, pore structure, crystalline property, and hydrophobicity with the presence of inflection point, the exposure stage must have an impact on membrane performance. The results of the MD test including permeate flux and conductivity are presented in Figure 7. A significantly increasing trend can be found as the exposure duration was higher than the inflection point, while before it, the flux showed no apparent variation. A flux of 31.23 kg/m²·h was achieved for membrane M8; however, the conductivity increased quickly and achieved 187 μS/cm after 2 h operation. Thus, although the flux of M8 and M9 was high, they are not suitable for the MD process due to the pore-

Table 4. Comparison with Other Hydrophobic Flat-Sheet Membranes by Different Polymer Material and Preparation Technology for DCMD Process

membrane	preparation method	feed solution			permeate solution			salt rejection /permeate conductivity	sustainability	refs
		types ^a	temp. ^b (°C)	flux (L/h)	temp. (°C)	flux (L/h)	permeate flux (kg/m ² ·h)			
PVDF	D-WPI	35 g/L	50	70	20	70	12.5	7.5	240 h, flux maintain at 12.5 kg/m ² ·h, conductivity stabilized at 5.3–7.5 μS/cm	48
¹ PVDF	commercial, CF ₄ plasma modified	4%	57.8	0.17 m/s	21.1	0.17 m/s	23.47	99.97%	-	24
² PVDF	commercial, Ar modified						16.68			
PVDF	VIPS	35 g/L	73	54	25	54	18.9	7.45 μS/cm	6 h, flux decreased by 4.3%, rejection maintained at over 99.7%	49
PVDF	electrospinning	3.5 wt %	50	36	20	36	20.6 ^c	<5 μS/cm	15 h, flux decreased by 21.7%, conductivity lower than 5 μS/cm	6
PTFE	commercial	10 g/L	60	31.3	20	31.3	32	-	-	50
PTFE	commercial, plasma modified	30 g/L	50	15	20	12	4	99.98%	-	51
PVDF-TFE	D-WPI	0.3 M	55	22	25	12	2.5	100%	-	52
PVDF-HFP	electrospinning	35 g/L	60	48	20	48	18.9	<5 μS/cm	50 h, flux maintained at 18.9 kg/m ² ·h, conductivity lower than 5 μS/cm.	8
PVDF-HFP	D-WPI	0.1 M	65	-	25	-	4.41	95.85%	-	53
PVDF-HFP/PAN	electrospinning	DI water	60	24	20	24	45	>98.5%	-	54
PES (CF ₄ plasma modified)	commercial, CF ₄ plasma modified	4 wt %	63.3	0.36 m/s	20	0.36 m/s	45.4	99.80%	55 h, flux stayed around 39 kg/m ² ·h after 40 h, then decreased to 36.4 kg/m ² ·h; conductivity decreased from 7.81 to 7.45 μS/cm.	55
PSf	VIPS	35 g/L	73	108	25	27	30	16 μS/cm	feed flux change to 27 °C 90 h, flux decreased by 3.5%, conductivity maintain lower than 40 μS/cm	56
PSf	LIPS, CF ₄ plasma modified	DI	70.3	0.17	20	0.17	53.33	100%	27 h, flux decreased by 10%, conductivity lower than 4 μS/cm.	57
PVDF-CTFE	D-WPI	35 g/L	55	65	25	50	28.32	9 μS/cm (99.98%)	48 h, flux higher than 21 kg/m ² ·h, conductivity kept lower than 20 μS/cm	this work

^aThe feed solution is NaCl solution, which only the concentration is listed if there is no detailed description. ^bTemp. represents the temperature. ^cData obtained from figures in literature; - = detailed data was missing.

wetting issue. The hydrophobic membrane permeability was strongly related to the pore size and pore interconnectivity, while the rejection was related to pore size and hydrophobicity. To prevent pore-wetting issue, a membrane with a higher hydrophobicity can sustain a larger pore and vice versa. That means a boundary of pore size theoretically existed for a membrane material with a fixed hydrophobicity. For M8 and M9, the pore size may be so large that exceeding the biggest pore size the membrane can sustain with certain hydrophobicity, though the hydrophobicity of both were relatively high (CA_{water} of 102° and 105° for M8 and M9 as shown in Table 2).

Membrane M7 under 300 s exposure duration seems to be the optimal membrane in this work, with a permeate flux of $28.43 \text{ kg/m}^2\cdot\text{h}$ and conductivity of $20 \mu\text{S/cm}$ (salt rejection = 99.96%). In this regard, this membrane was applied to a continuous 48 h MD test to study the sustainability, and the result is presented in Figure 8. It can be found that the conductivity decreased quickly especially in the first 2 h, indicating permeate with high flux and low conductivity. The permeate conductivity was $9 \mu\text{S/cm}$ after 22 h operation, which can be considered as the permeate conductivity with an assumption that original distilled water was totally discharged. The conductivity increased gradually 26 h later, which may be the result of pore wetting. However, the conductivity was kept lower than $20 \mu\text{S/cm}$ during the 48 h continuous operation, and the rejection was still higher than 99.95%. Meanwhile, the permeate flux was kept constant in the first 20 h, and then it decreased by less than 25%, which was still kept higher than $21 \text{ kg/m}^2\cdot\text{h}$ during the whole operation. The relatively high hydrophobicity, high roughness, narrow pore distribution, but interconnected pore structure was believed to be the reason for the excellent performance of the membrane M7 as discussed.

Comparison with Hydrophobic Membranes Applied in the MD Process in the Literature. A comparison with other hydrophobic polymer membranes for DCMD application reported in recent years was carried out and is listed in Table 4.^{6,8,25,48–57} It can be found that the PVDF-CTFE membrane prepared in this work presented a competitive advantage in permeate flux with other reported hydrophobic membrane, although some of them have been carefully hydrophobically modified. As to the membrane sustainability, the permeate flux and the conductivity of the PVDF-CTFE membrane in this work were kept stable during the 48 h operation, which also showed certain advantages as compared to some previous research. It was safe to say that PVDF-CTFE copolymer has noteworthy potential for hydrophobic membrane preparation and application, especially when more efforts have been paid to prepare and modify the membrane.

CONCLUSIONS

In the present work, PVDF-CTFE hydrophobic flat-sheet membranes with a biomimetic surface and interconnected pore structure were manufactured by a facile two-stage phase inversion method (i.e., EIPS and DIPS) for the first time. The phase inversion process during membrane formation was controlled by tuning the duration of the exposure stage to acquire an ideal structure. It was found that the exposure stage benefited crystallization due to the solvent evaporation-induced phase inversion in air, which indicates that the S–L demixing process can be controlled by tuning the exposure duration. The biomimetic surface and interconnected pore structure can be expected due to the gelation/crystallization, which has been

evidenced by membrane crystallinity. Meanwhile, an inflection point (i.e., 300 s) was observed in this work, above which the drastic variation would appear. The MD flux showed an agreement with the pore size, while the rejection possessed a reverse trend. M7 with 300 s air exposure is the optimal membrane with a permeate flux of $28.43 \text{ kg/m}^2\cdot\text{h}$ and a conductivity of $9 \mu\text{S/cm}$, which also had a relatively stable performance during a 48 h continuous MD operation.

The results presented in this work clearly demonstrated that a two-stage phase inversion process happens in the air-casting and immersion processes, which has a significant influence on membrane morphology, structure, properties, and performance. It also surely believed that membrane with biomimetic hydrophobic structure and excellent interconnectivity can be expected by carefully controlling the phase inversion process during membrane formation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsami.6b11249](https://doi.org/10.1021/acsami.6b11249).

Surface pore structure study by image-pro-plus 6.0 and image J, overall porosity measurement, overall pore size and pore distribution by capillary flow method, DCMD process; schematic diagram of the DCMD setup and design diagram of the flat-sheet membrane module, membrane surface depth distribution image by AFM, membrane surface morphology plotted by grayscale values of SEM images, SEM micrographs of membrane surface for pore structure analysis, SEM micrographs of membrane cross-section; Surface roughness of PVDF-CTFE membranes, pore size of PVDF-CTFE membranes (PDF)

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Notes

The authors declare no competing financial interest.

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