Post-fabrication modification of electrospun nanofiber mats with polymer coating for membrane distillation applications

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Abstract

Post-treatment of electrospun nanofibers is a versatile and scalable approach for the fabrication of membranes with controlled pore size, porosity, and morphology. In this study, we demonstrate a novel solution-based approach for the fabrication of membrane distillation (MD) membranes with adjustable pore size and performance through non-solvent induced phase separation of a polymeric solution over an electrospun fiber mat. Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) was dissolved in a blend of acetone and dimethylacetamide and used to produce a highly porous electrospun fiber mat with an average pore diameter of $\sim 1.2 \mu\text{m}$. Surface coating of the PVDF-HFP nanofibers with polyvinylidene fluoride (PVDF) through phase separation enabled control of the membrane pore size by filling the empty domains between the fibers. The coated fiber mats were characterized for their surface hydrophobicity, porosity, and structure. The PVDF polymeric coating layer integrated within the electrospun mat decreased the average pore diameter to $< 0.6 \mu\text{m}$ without compromising the surface hydrophobicity. By controlling the depth of the PVDF coating layer within the substrate, we were able to fabricate robust membranes with near complete salt rejection ($> 99.9\%$) and a water flux of $30 \text{ L m}^{-2} \text{ h}^{-1}$ in direct contact MD experiments with 40°C temperature difference between the feed and permeate solutions. This coating procedure is compatible with current roll-to-roll membrane fabrication processes, making it a viable approach for large-scale fabrication of electrospun membranes with exceptional performance for MD applications.

Keywords: Membrane distillation; Electrospun fiber mats; Asymmetric membrane; Microporous membranes for MD; Adjustable pore size

1. Introduction

Membrane distillation (MD) is an emerging separation process with potential applications for desalination of high salinity source waters [1, 2]. MD can also be integrated with other processes to convert low-grade heat to electric power [3, 4] or for treatment of complex wastewaters [5-9]. Unlike conventional thermal desalination processes, which require high operating temperatures, MD can use a small temperature difference between a hot feed and a cold permeate to achieve a vapor pressure driving force across the membrane [10, 11]. The vapor pressure of water is weakly dependent on the feed water salinity [12], allowing MD to desalinate hypersaline source water that cannot be treated by pressure-driven membrane processes, such as reverse osmosis (RO).

To achieve optimal performance, MD membranes should have two key properties: (i) high porosity to maximize water vapor flux and (ii) high hydrophobicity to avoid membrane pore wetting. Fabrication of high-performance MD membranes that meet these criteria via scalable and low-cost manufacturing techniques is a major technical challenge for the commercialization of MD technology, as current MD membranes still suffer from low permeate water flux and frequent pore wetting due to low hydrophobicity [13]. While novel membrane designs can overcome these limitations, such membranes must be fabricated using a scalable, environmentally benign, and low-cost technique.

Electrospun polymer nanofibers exhibit excellent characteristics suitable for MD applications, such as high surface roughness, high porosity, and mechanical robustness [14]. The ability to fabricate fibers with different morphology using various polymers renders this technology promising for a wide range of applications, from electronic devices to membrane filters and biomedical materials [15-19]. Previous studies have shown the feasibility of fabricating membranes, suitable for use in MD, using electrospinning of hydrophobic polymers, including polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) [20, 21].

PVDF-HFP exhibits low surface energy [22, 23], which makes it an attractive material for the fabrication of MD membranes with improved hydrophobicity [24]. Additionally, electrospun nanofiber mats exhibit high surface roughness, which results in an increased air gap at the surface interface, and thus enhances surface hydrophobicity. These promising features render

electrospun fiber mats prepared using PVDF-HFP a suitable platform to fabricate high-performance MD membrane.

Due to the random assembly of fibers and the lack of chemical bonding between them, fine control of the membrane structure, including pore size and pore size distribution, is not achievable by electrospinning [24]. To address these limitations, electrospun mats were treated post-fabrication using hot pressing [20, 25], which fuses the fibers on the top layer together and reduces the overall membrane porosity and surface roughness. However, the latter compromises the surface hydrophobicity, thereby increasing the wetting propensity of the membrane. Alternative strategies that allow fine-tuning of the porosity and structural integrity of nanofiber mats would thus represent a significant step toward the development of more efficient electrospun nanofiber MD membranes.

In this study, we developed a simple and scalable method to fabricate robust MD membranes based on electrospun nanofibers. We prepared an electrospun PVDF-HFP fiber mat substrate and then applied a PVDF coating on the fibers using a simple phase inversion approach. The additional polymer coating not only decreases the pore size and the porosity but also links the fibers, which substantially improves the mechanical stability of the fiber mat. The fabricated membranes demonstrated a relatively high water flux and nearly complete salt rejection in a direct contact membrane distillation (DCMD) test. Our results highlight the potential of this method for scalable production of membranes for membrane distillation applications.

2. Materials and methods

2.1. Materials and chemicals

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) (*MW*: 455 kDa), polyvinylidene fluoride (PVDF) (*MW*: 275 kDa), *N,N*-Dimethylacetamide (DMAc) (99.5%), and triethyl phosphate (TEP) (99.8%) were purchased from Sigma-Aldrich and used as received. Acetone (99.5%) and 2-propanol (99.5%) were acquired from J. T. Baker (Phillipsburg, NJ). Ultrapure water was obtained from a Millipore Milli-Q system.

2.2. PVDF-HFP substrate fabrication

1/10 (w/v) PVDF-HFP in a 4/6 (v/v) mixture of DMAc and acetone was prepared by dissolving the polymer in the solvent at room temperature under overnight stirring. A 10 mL PVDF-HFP solution was loaded in a Luer-Lok Tip syringe (Becton Dickinson & Co., Franklin Lakes, NJ), to which an 18 G $\times$ 1 inch precision glide needle (Becton Dickinson & Co.) was attached. The syringe was placed horizontally on the syringe pump (Harvard Apparatus, Plymouth Meeting, PA), and an electrode of high-voltage supply (Gamma High Voltage Research Inc., Ormond Beach, FL) was clamped to the needle tip. The needle to collector distance was kept at 15 cm. A 10.5 cm $\times$ 38.5 cm aluminum foil was installed on a rotating drum which moved at a speed of $\sim$ 16 cm/min to collect the fibers. The flow rate and the applied voltage were set to 1 mL/h and 18.5 kV, respectively. The electrospinning was performed in a closed chamber under controlled temperature (30 $^{\circ}$ C) and relative humidity (45-50%). Fibers were collected for 10 hours, and the collected fiber mat was dried in an oven at 60 $^{\circ}$ C for 12 hours.

2.3 PVDF coating of the substrate

A 15% (w/v) PVDF solution was prepared by mixing a known amount of polymer in TEP at 70 $^{\circ}$ C and continuous stirring for 8 hours. The solution was cooled to room temperature before use. The prepared PVDF solution was loaded on an aluminum rod by rolling it on a glass plate covered with the polymer solution. Then, this PVDF-impregnated rod was rolled on the PVDF-HFP electrospun substrate to achieve a thin layer PVDF coating. Immediately after PVDF coating, the substrate was submerged in a 2-propanol coagulation bath to induce phase inversion of the PVDF, as illustrated in Fig. 1. For the thick PVDF layer coating, the PVDF solution was spread on the PVDF-HFP electrospun substrate using a doctor blade casting knife and allowed to penetrate all the way through the fiber mat. PVDF-coated PVDF-HFP electrospun substrates on a glass plate were left for 20 minutes in the coagulation bath to induce phase inversion, and then transferred to a water bath where they were stored overnight to remove the residual solvent. After solvent removal, the membranes were dried in an oven at 60 $^{\circ}$ C for 24 hours.

Fig. 1. Schematic of the process for controlled infiltration of the PVDF dope solution (i.e., PVDF dissolved in TEP) within the PVDF-HFP electrospun nanofiber mat and thin layer coating of the nanofiber mats by non-solvent induced phase separation. Step 1: Thin layer of PVDF solution is loaded onto aluminum rod. Step 2: The PVDF solution layer is transferred to the fiber mat. Step 3: The fiber mat coated with dope solution is submerged in a coagulation bath for phase separation of the PVDF coating layer.

2.4 Membrane characterization

2.4.1 X-ray photoelectron spectroscopy (XPS)

XPS was performed on a Physical Electronics instrument (PHI 5000, VersaProbe) with a scanning monochromatic source from an Al anode with dual beam charge neutralization. Both survey and high-resolution spectra were acquired over a spot of approximately 200 μm in

diameter with ~50 W beam power. High-resolution XPS spectra of C1s were acquired with 0.1 eV resolution at 23.5 eV pass energy with 200 ms dwell time, and averaged over 10 scans.

2.4.2 Scanning electron microscopy

All micrographs were acquired using a Hitachi Ultra-High-Resolution Analytical Field Emission Scanning Electron Microscope (FE-SEM) SU-70. To obtain cross-section images, membranes were dried at room temperature and freeze-fractured using liquid nitrogen before mounting on the sample holder. A Denton chromium sputtering machine equipped with a quartz crystal sensor and film deposition monitor (INFICON) was used to coat the sample surface with a 15 nm thick chromium layer. The coated samples were immediately imaged to avoid oxidation of the conductive coating.

2.4.3 Transmission electron microscopy (TEM)

For TEM imaging, nanofibers were immersed in epoxy resin (EMbed 812, Electron Microscopy Sciences, Hatfield, PA) and deaerated for 4 hours at room temperature under vacuum. The samples were cured at 58 °C for 48 hours. Embedded samples were cut into 0.07 µm slices and placed on a copper grid (Holey Carbon, 300 mesh, Electron Microscopy Sciences, Hatfield, PA). Samples were visualized with an FEI Tecnai Osiris microscope (FEI, Hillsboro, OR), operating at an acceleration voltage of 200 kV. Elemental mapping was performed by solid-angle X-ray spectroscopy.

2.4.4 Contact angle

Water contact angles for the top and bottom sides of the membranes were measured by an optical tensiometer (OneAttension, Biolin scientific instrument) using the sessile drop method. A 3-µL DI water droplet was placed on the air-dried membrane sample and photographed using a digital camera. The left and right contact angles were determined from digital images with post-processing software (OneAttension software). Measurement for each data point was conducted at three different locations on the same membrane coupon and averaged.

2.4.5 Pore size distribution

The pore size distribution was evaluated by the wet/dry flow method [26] using a custom-made porometer setup (Fig. S1), which uses a small gas-filtration unit with a stainless steel filter holder (KS 25A, Advantec MFS) having an effective area of ~3.9 cm² (50% open). The

membrane was cut to fit the holder size. A commercial wetting liquid (Porefil), having a low surface tension (16 mN/m) and vapor pressure (399 Pa at 298 K), was used to wet the membrane. A digital pressure regulator (Control Air Inc., 900-CHA) was used to control the nitrogen gas pressure, and gas flow and pressure across the membrane were recorded by a pressure transducer (Honeywell, px2an1xx100psaax) and a flow meter (Porter MPC20).

2.4.6 Porosity

Film porosity was estimated by a gravimetric method. The oven-dried membrane was weighed and subsequently submerged in a container filled with 2-propanol for one hour. The wet membrane was taken out of the 2-propanol, sandwiched between nylon fabrics (VWR), and further padded with paper wipes to remove the excess 2-propanol from the surface. Wet sample weight was monitored using an analytical balance (Denver PI-214A). The weight decrease was recorded to a laptop in one-second intervals until the sample was fully dried, and no changes in weight were observed. The porosity (ε) was estimated using the equation:

$$\varepsilon = \frac{V_{pore}}{V_{total}} = \frac{\frac{m_{IPA}}{\rho_{IPA}}}{V_{pore} + V_{Polymer}} = \frac{\frac{m_{IPA}}{\rho_{IPA}}}{\frac{m_{IPA}}{\rho_{IPA}} + \frac{m_{Polymer}}{\rho_{Polymer}}} \quad (1)$$

where V , m , and ρ are the volume, mass, and density, respectively, and IPA indicates the 2-propanol. The test was performed three times, and the porosity values were averaged.

2.4.7 Liquid Entry Pressure

The liquid entry pressure (LEP) was measured using the porometer previously described. DI water was placed on the membrane and the pressure in the sample holder was increased by flowing nitrogen gas. As the applied pressure increases, the gas pushes the water out of the membrane pores. The pressure at which the gas flow is detected by a flow meter was reported as the liquid entry pressure.

2.4.8 tensile test

We evaluated the mechanical properties of the electrospun PVDF-HFP membranes using a tensile tester (Series 5542, Instron, MA). A membrane sample (1 cm $\times$ 3 cm) was vertically

mounted on the tester using two grippers at its ends, leaving a 2 cm-gauge length for mechanical loading. Load-deformation data were recorded at a rate of 0.5 mm/sec.

2.5 Evaluation of Membrane Performance

The performance of fabricated membranes was evaluated using a laboratory-scale direct contact membrane distillation (DCMD) unit (Fig. S2). The membranes were inserted into the custom-built acrylic cell with an effective membrane area of 20.02 cm² for both distillate (permeate) and feed sides. Hot feed and cold distillate streams were circulated using two variable gear pumps (Cole-Parmer, Vernon Hills, IL) and the temperatures were kept constant at 60 and 20 °C, respectively, using two recirculating water baths (Polystat Standard, Cole-Parmer, Vernon Hills, IL) [27]. Spacers were inserted in both feed and distillate channels to support and maintain the membrane geometry in the cell. The applied feed cross flow velocity was two times higher than permeate stream (i.e., 15.2 cm/s for feed versus 7.6 cm/s for permeate) to facilitate the detection of membrane wetting by imposing a slightly higher hydraulic pressure on the feed side. Water vapor flux, J_w , across the membrane was measured by monitoring the increase in distillate mass using a digital balance (CUW 6200H, CAS). The distillate weight gain was recorded in a laptop at one-minute intervals. Salt passage was monitored by measuring the salt concentration in distillate using a calibrated conductivity meter (Oakton Instruments, Vernon Hills, IL) at one-minute intervals.

3. Results and discussion

3.1 Membrane Structure

The control substrate was prepared by electrospinning a solution of PVDF-HFP in a mixture of DMAc and acetone [28]. An electrospun fiber mat composed of nanofibers with an average diameter of 477 nm and an overall thickness of 70 μm was collected on an aluminum foil. We gained control of the effective pore diameter of the fabricated membranes by controlling the infiltration depth of a PVDF solution within the fiber mat, followed by solidifying the polymer by phase inversion. TEP (i.e., the solvent used for PVDF coating solution) does not dissolve PVDF-HFP at room temperature, which enables PVDF coating on the PVDF-HFP electrospun fibers without damaging the fibers.

Two different polymer coating approaches were used to control the penetration depth of the dope solution within the substrate and, consequently, the thickness of the polymer (PVDF) film deposited within the fiber mat. In the first approach, a PVDF solution in TEP was spread evenly on the PVDF-HFP fiber mats using a knife casting blade, which resulted in a deep penetration of the polymer solution inside the fiber mat. For the second approach, the amount of PVDF applied to the fiber mat was controlled by wetting a rolling rod uniformly with a known amount of polymer solution. By rolling the rod against the fiber mat, the solution was transferred to the substrate. The high porosity of the substrate, combined with the low surface tension of the PVDF in TEP solution (38.2 and ~36.5 mN/m for TEP and PVDF, respectively [29]), results in effective permeation of the polymer solution into the substrate pores by capillary action [30].

The PVDF-coated fiber mat was subsequently submerged in the coagulation bath to precipitate PVDF on the fibers via phase separation. During the phase separation process, the solid polymer structure collapses within the substrate voids. As a result, most of the polymer coats the nanofibers and less remains within the voids between fibers.

The change in membrane morphology after PVDF coating is visualized by scanning electron microscopy (SEM). Figs. 2A and 2B show that the penetration depth of the polymer solution within the electrospun mat was significantly different for the two different coating approaches, as indicated by the depth of the solid PVDF residual, visible within the fiber mat. The control over the penetration depth of dope solution within the substrate provides a simple route to manipulate the membrane structure. The ease of processing can make this method a viable approach to fabricating membranes in a roll-to-roll fashion [31].

Fig. 2. Morphology of the PVDF-HFP electrospun fiber mats after coating with PVDF via a thin layer casting method and a knife casting method. The SEM micrographs (A) and (B) are cross sections, (C) and (D) are top surfaces, and (E) and (F) are bottom surfaces of the modified PVDF-HFP electrospun fiber mats. The red arrows in parts (A) and (B) indicate penetration depth of the PVDF coating solution. The insets in parts (A) and (B) are high-magnification images and scale bars indicate 1 μm .

Due to a low solubility parameter of the PVDF–2-propanol (nonsolvent coagulation medium) pair (i.e., 9.7 MPa^{0.5}), the liquid-liquid de-mixing is delayed and the formation of a dense skin layer is prevented [32–34]. As shown in Fig. 2C, when the dope solution penetration depth was limited to 10–20 μm from the top of the mat, a relatively homogeneous PVDF coating around the fibers was formed upon phase inversion. In contrast, when the knife casting method was used,

crystalline domains, visible as micron-sized particles (Fig. 2D), were formed on the top. These crystalline domains are attributed to the phase inversion of PVDF by the soft coagulation medium (i.e., 2-propanol) as shown in previous studies [35, 36].

The bottom surface of the mat was also visualized to verify the penetration depth of the PVDF solution. When the dope solution penetration is controlled, the morphology of the fiber on the bottom side of the electrospun mat remains intact, demonstrating a thin layer PVDF coating within a confined thin layer of the PVDF-HFP substrate (Fig. 2E). On the other hand, when PVDF is spread on the fiber mat using a casting knife, the polymer solution penetrates deep into the mat. Consequently, as shown in Fig. 2F, the bottom side of the membrane contains smooth patches that are indicative of PVDF phase inversion at the interface between a glass plate and the substrate surface. As shown in the cross-sectional SEM (Fig. 2A), when the penetration depth of the polymer solution is confined within the porous substrate, the final membrane structure is asymmetric. The asymmetric membrane structure is crucial for MD performance, as discussed later in Section 3.5 [34, 37].

To further confirm the PVDF coating on the PVDF-HFP electrospun fibers, we visualized the cross section of the fibers by TEM imaging. The nanofibers were embedded in an epoxy resin and microtomed into 70 nm thin-slices. An additional PVDF layer was observed around the fibers upon non-solvent induced phase inversion (Fig. 3). Images also indicate that polymer residues occupy the space between individual fibers and create a stable linkage between them, which can be easily observed when the fibers are closer to each other (Figs. 3B and 3D). This PVDF bridging between fibers substantially improves the mechanical stability of the mat, as we discuss later.

Fig. 3. Transmission electron micrographs of the fiber cross-section showing the coated and uncoated fiber morphology. Electrospun PVDF-HFP fibers (A, C) show a well-defined round morphology while PVDF-coated fibers have a polymeric web-like structure bridging the fibers (B, D).

3.2 Membrane porosity and pore size distribution

The pore size distribution was evaluated by a wet/dry flow method with perfluoroether (Porefil, Porometer, Belgium) as a wetting liquid using a lab-made porometer (Fig. S1). Due to the low surface tension (16 mN/m), Porefil can fully wet the membrane, such that the contact angle between the membrane surface and the wetting liquid, θ , is assumed to be zero. The membrane pore diameter, d_p , was calculated using the Laplace equation [26]:

$$d_p = \frac{4\sigma}{\Delta P} \cos \theta \quad (2)$$

where ΔP is the pressure difference across the membrane and σ is the surface tension of the wetting liquid. The additional polymer coating around the fibers was found to decrease the effective pore size of the membrane, as observed by a shift of the pore diameter distribution towards smaller values (Fig. 4). Also, the deeper penetration of the PVDF solution into the fiber mat resulted in a narrower pore size distribution. The results suggest that the effective pore size distribution can be tuned by adjusting the penetration depth of the polymer coating solution. To enhance the versatility of this technique and gain better control over the pore size, other phase inversion parameters, including the viscosity of the dope solution and coagulation bath media, can be further examined [38-40].

Fig. 4. Pore size distributions of (A) control PVDF-HFP electrospun substrate, (B) PVDF-HFP substrate modified with a shallow penetration of PVDF dope solution, and (C) PVDF-HFP

substrate modified with a deep penetration of PVDF dope solution. Pore size distribution was measured by a wet/dry capillary flow method using a custom-built porometer.

The porosities of the control and modified membranes are provided in Table 1. It is evident that the overall membrane porosity is reduced as the polymer loading within the fiber mat is increased [41, 42]. This reduction in porosity is expected, because the void volume between the fibers is occupied by the PVDF coating through phase separation. The decrease in porosity was proportional to the thickness of the coating layer. The porosities of the control, thin layer casting, and knife casting modified membranes were estimated to be 90.6, 80.2, and 70.2%, respectively.

Table 1. Effect of infiltration depth of dope solution on the properties of the electrospun substrate.

	Contact Angle (°)		Porosity, ϵ (%)	Liquid Entry Pressure (kPa)	Tensile measurement		Total thickness (μm)
	Top	Bottom			Max. Force (N)	Max. Strain (mm)	
Control	131.9 ± 2.0		90.6 ± 0.6	56	2.38 ± 0.24	16.9 ± 3.28	77
Thin layer	130.6 ± 1.1	132.1 ± 1.7	80.2 ± 0.3	163	3.38 ± 0.13	24.2 ± 1.41	75
Casting knife	133.3 ± 1.7	126.9 ± 2.4	70.2 ± 0.2	325	2.78 ± 0.09	2.1 ± 1.34	71

3.3 Membrane surface chemical and wetting properties

X-ray photoelectron spectroscopy (XPS) analysis was performed on the control and modified PVDF-HFP electrospun fiber mats to elucidate the surface chemistry of the membrane before and after polymer coating. As shown in Fig. 5A, the C1s spectrum of the control PVDF-HFP nanofibers exhibits two major peaks attributable to the fluorinated carbon species and one peak ascribed to the hydrocarbon species. The peaks at 293.2 and 290.6 eV are assigned to the CF_3 and CF_2 species, respectively, and the peak at 286.4 eV is ascribed to the CH_2 moiety of the PVDF block. The appearance of peaks at 284.6, 285.8, and 286.5 eV in the C1s spectrum was attributed to adventitious carbon contamination present in the environment [43]. As shown in Fig. 5A, the concentration of CF_3 species is significantly smaller compared to the CF_2 species. Under

humid electrospinning conditions, it was expected that the HFP block orientation would be inward in order to minimize the surface energy. This inward orientation can explain the significant mismatch between the stoichiometry ratio of the CF_3 in PVDF-HFP and the measured CF_3 concentration on the surface of the control sample.

Fig. 5B shows the C1s spectrum of the PVDF-coated PVDF-HFP electrospun fibers. Upon coating of the fiber with PVDF, the CF_3 peak at 293.2 eV completely vanished, and the most prominent features of the spectrum were assigned to the PVDF layer. The minimal change in the XPS spectrum of the sample after coating suggests that the PVDF coating has minor influence on the chemical composition of the membrane surface.

Fig. 5. X-ray photoelectron spectroscopy spectrum showing the C1s region of the (A) electrospun fiber mat and (B) fiber mat after post processing. The unlabeled peaks are attributed to the adventitious carbon contamination, which has an overlap with the range, in which the CF binding energy range is present in PVDF-HFP.

As indicated earlier, surface hydrophobicity or wettability of the membrane is dependent on its surface energy and surface roughness [44-46]. To evaluate surface hydrophobicity, we measured the water contact angle of the membranes using the sessile drop method (Table 1) [47].

Interestingly, no significant difference was observed between the contact angles of the control PVDF-HFP substrate (131.9°) and the PVDF-HFP fiber mat modified with a thin layer PVDF coating (130.6°). This observation, along with the minimal difference in the chemical composition (based on XPS analysis) of the PVDF-HFP electrospun fiber mats before and after PVDF coating, suggests that membrane surface roughness has not been significantly influenced by the thin layer PVDF coating.

The water contact angle on the top surface of the PVDF-HFP electrospun mat coated with a thick PVDF layer by a knife casting method was 133.3° , higher than the control and the thin layer modified PVDF-HFP electrospun fiber mats. For the membranes modified with a knife casting technique, a globular crystalline polymer domain on the top layer (shown in Figure 2D) is expected to introduce additional surface roughness, thereby resulting in enhanced surface hydrophobicity. The water contact angle on the bottom side of this membrane was smaller than the control PVDF-HFP substrate (127° and 132° for the thin layer modified and the control PVDF-HFP electrospun mats, respectively). This difference can be explained by a smoother surface morphology, shown in Figure 2 F, created by PVDF penetration and deposition at the glass plate substrate and fiber interface.

3.4 Membrane liquid entry pressure and mechanical properties

We also measured the membrane liquid entry pressure for water (LEP_w), defined as the minimum pressure required to break the water meniscus at the membrane pore opening [48], which leads to pore wetting. The LEP_w is influenced by the effective solid-liquid contact angle, the membrane pore size, and the pore shape, as described by the Laplace equation [49, 50]. The correlation between a rougher surface and higher contact angle is straightforward under the non-wetting Cassie–Baxter state. An increase in surface roughness leads to higher contact angle and, correspondingly, a higher LEP of a membranes with the same pore size [51, 52]. Because the changes in membrane surface hydrophobicity were relatively small, as evidenced by previously discussed contact angle measurements, the differences in LEP_w can be explained by the change in the pore size distribution of the membranes [26]. As expected, a decrease in the maximum pore size leads to an increase in LEP_w. The LEP_w values for the control electrospun substrate

and thin layer and knife casting modified membranes were 56, 163, and 325 kPa, respectively (Table 1), which is in line with the observed shift in the pore size distribution (Fig. 4).

Tensile tests were performed to evaluate the effect of the PVDF coating on the mechanical properties of the membrane. Results from tensile tests are presented in Fig. S5 of the Supplementary Data and are also summarized in Table 1. We found that a thick coating layer achieved by a knife casting method increased the maximum tensile strength of the electrospun fiber mats by 16.8%. However, this thick polymer coating inhibited the ability of the fibers to strain and thus decreased the maximum strain by 80.4%. In contrast, thin layer PVDF coating linked fibers together without compromising the fiber flexibility, resulting in improvements of both maximum strain and strength of the membrane by 43.2 and 42%, respectively.

3.5 Membrane performance

The performance of the control and modified membranes was evaluated using a laboratory-scale direct contact membrane distillation (DCMD) unit (Fig. S2). Hot feed and cold distillate streams were circulated at temperatures of 60 and 20° C, respectively. Distillate flux, J_w , across the membrane was measured by monitoring the increase in distillate mass using a digital balance, and salt passage was monitored by the change in salt concentration of the distillate using an electric conductivity meter.

We performed DCMD experiments at a feed cross-flow velocity two times higher than the permeate stream (i.e., 15.2 cm/s for feed versus 7.6 cm/s for permeate) to facilitate membrane wetting within a relatively short testing time by imposing a slightly higher hydraulic pressure on the feed side. The control PVDF-HFP electrospun substrate produced very high permeate flux; however, the presence of relatively large pores caused rapid wetting of the membrane (Fig. 6A). The conductivity of the distillate for the control membrane started to increase exponentially 30 minutes after the onset of the DCMD experiment, clearly indicating wetting of the membrane.

On the other hand, the membranes with PVDF coating exhibited stable DCMD performance with a negligible change in distillate conductivity (Figs. 6B and 6C). Coating the electrospun fiber substrate with PVDF decreased the effective pore size (Fig. 4) without compromising surface hydrophobicity (Table 1), thereby resulting in higher membrane wetting resistance. This enhanced wetting resistance of the PVDF-coated electrospun substrates enabled a stable

desalination performance under MD operation conditions that facilitate wetting (i.e., two times higher feed cross flow velocity than distillate stream).

While the salt rejection has been significantly improved after PVDF coating, the decrease in pore size (Fig. 4) and porosity (Table 1) following the post-fabrication modification negatively impacted the membrane water vapor flux[53]. Comparing membrane flux performance (Fig. 6) and membrane physical properties (Table 1) clearly showed that thicker PVDF coatings on the PVDF-HFP substrates resulted in a lower water vapor flux. The highly porous (~90%) control electrospun mats exhibited a high water flux of $\sim 70 \text{ L m}^{-2} \text{ h}^{-1}$, while membranes coated through a thin layer and a knife casting methods showed lower water fluxes of ~ 30 and $\sim 10 \text{ L m}^{-2} \text{ h}^{-1}$, respectively.

Although additional polymer coating reduced water vapor permeability, the membrane modified with a thin layer coating still exhibited a fairly high water flux of $\sim 30 \text{ L m}^{-2} \text{ h}^{-1}$. The thin layer modified membrane also showed stable desalination performance in a long-term (12 hours) DCMD experiment (Fig. S3 of the Supplementary Data). We attribute the observed high MD performance of the thin layer modified membrane to its unique structural properties. As shown previously, a thin polymer coating allows for the control of the pore size of the electrospun substrate without a significant reduction in porosity, producing membranes with an asymmetric structure (i.e., a dense layer on top of a highly porous substrate). The reduced pore size of the membrane top layer contributes to increasing LEP, thereby enhancing surface wetting resistance, while a highly porous substrate minimizes resistance to water vapor transport, resulting in high water permeability.

Fig. 6. Water flux and solution conductivity change in the permeate collector reservoir, evaluated using a laboratory-scale direct contact membrane distillation (DCMD) unit. (A) PVDF-HFP electrospun nanofibers (control). (B) PVDF-HFP electrospun nanofibers modified by shallow infiltration of the dope solution followed by phase inversion. (C) PVDF-HFP electrospun nanofibers modified by deep infiltration of the dope solution followed by phase inversion. Experimental conditions were as follows: feed solution of 1 M NaCl, feed and distillate crossflow velocities of 15.2 and 7.6 cm/s, and feed and distillate temperatures of 60 and 20 °C, respectively.

4. Conclusion

We developed a method to integrate polymeric materials within a highly porous electrospun mat for MD membrane fabrication. Controlling the penetration depth of the dope solution, and, consequently, the thickness of the polymeric coating layer on the electrospun substrate allows for tunable membrane structural parameters and performance without compromising surface hydrophobicity. Proper choice for a solvent which does not damage the polymeric fibers and control over the polymer loading were found to be important factors that enabled membrane properties suitable for MD application. The electrospun fiber substrates coated with a controlled polymeric layer thickness exhibited stable desalination performance in MD due to the enhanced surface wetting resistance. The proposed coating technique is suitable for large scale electrospun

membrane fabrication for a wide range of other applications, including size-based air and water filtration systems.

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References

- [1] P. Wang, T.-S. Chung, Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring, *Journal of Membrane Science*, 474 (2015) 39-56.
- [2] P. Wang, Y. Cui, Q. Ge, T.F. Tew, T.-S. Chung, Evaluation of hydroacid complex in the forward osmosis–membrane distillation (FO–MD) system for desalination, *Journal of Membrane Science*, 494 (2015) 1-7.
- [3] S. Lin, N.Y. Yip, T.Y. Cath, C.O. Osuji, M. Elimelech, Hybrid pressure retarded osmosis–membrane distillation system for power generation from low-grade heat: Thermodynamic analysis and energy efficiency, *Environmental science & technology*, 48 (2014) 5306-5313.
- [4] E. Shaulsky, C. Boo, S. Lin, M. Elimelech, Membrane-Based Osmotic Heat Engine with Organic Solvent for Enhanced Power Generation from Low-Grade Heat, *Environmental science & technology*, 49 (2015) 5820-5827.
- [5] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, A forward osmosis–membrane distillation hybrid process for direct sewer mining: system performance and limitations, *Environmental science & technology*, 47 (2013) 13486-13493.
- [6] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–membrane distillation process, *Environmental Science & Technology Letters*, 1 (2014) 191-195.
- [7] L.D. Tijging, Y.C. Woo, J.-S. Choi, S. Lee, S.-H. Kim, H.K. Shon, Fouling and its control in membrane distillation—a review, *Journal of Membrane Science*, 475 (2015) 215-244.
- [8] C. Boo, J. Lee, M. Elimelech, Engineering Surface Energy and Nanostructure of Microporous Films for Expanded Membrane Distillation Applications, *Environmental Science & Technology*, 50 (2016) 8112-8119.
- [9] J. Lee, C. Boo, W.-H. Ryu, A.D. Taylor, M. Elimelech, Development of Omniphobic Desalination Membranes Using a Charged Electrospun Nanofiber Scaffold, *ACS applied materials & interfaces*, 8 (2016) 11154-11161.
- [10] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, *Desalination*, 287 (2012) 2-18.

- [11] S. Lin, N.Y. Yip, M. Elimelech, Direct contact membrane distillation with heat recovery: Thermodynamic insights from module scale modeling, *Journal of Membrane Science*, 453 (2014) 498-515.
- [12] M. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, *J Membrane Sci*, 285 (2006) 4-29.
- [13] A. Alklaibi, N. Lior, Membrane-distillation desalination: status and potential, *Desalination*, 171 (2005) 111-131.
- [14] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, *Composites science and technology*, 63 (2003) 2223-2253.
- [15] J. Doshi, D.H. Reneker, Electrospinning process and applications of electrospun fibers, in: *Industry Applications Society Annual Meeting, 1993., Conference Record of the 1993 IEEE, IEEE, 1993*, pp. 1698-1703.
- [16] T.J. Sill, H.A. von Recum, Electrospinning: applications in drug delivery and tissue engineering, *Biomaterials*, 29 (2008) 1989-2006.
- [17] A.F. De Faria, F.o. Perreault, E. Shaulsky, L.H. Arias Chavez, M. Elimelech, Antimicrobial Electrospun Biopolymer Nanofiber Mats Functionalized with Graphene Oxide–Silver Nanocomposites, *ACS applied materials & interfaces*, 7 (2015) 12751-12759.
- [18] W.-H. Ryu, H. Wilson, S. Sohn, J. Li, X. Tong, E. Shaulsky, J. Schroers, M. Elimelech, A.D. Taylor, Heterogeneous WS_x/WO₃ Thorn-Bush Nanofiber Electrodes for Sodium-Ion Batteries, *ACS nano*, 10 (2016) 3257-3266.
- [19] C. Boo, J. Lee, M. Elimelech, Omniphobic Polyvinylidene Fluoride (PVDF) Membrane for Desalination of Shale Gas Produced Water by Membrane Distillation, *Environmental Science & Technology*, 50 (2016) 12275-12282.
- [20] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, *Journal of Membrane Science*, 425-426 (2013) 30-39.
- [21] Z. Dong, S.J. Kennedy, Y. Wu, Electrospinning materials for energy-related applications and devices, *Journal of Power Sources*, 196 (2011) 4886-4904.
- [22] P.-G. De Gennes, F. Brochard-Wyart, D. Quéré, *Capillarity and wetting phenomena: drops, bubbles, pearls, waves*, Springer Science & Business Media, 2013.
- [23] V.A. Ganesh, A.S. Nair, H.K. Raut, T.T.Y. Tan, C. He, S. Ramakrishna, J. Xu, Superhydrophobic fluorinated POSS–PVDF–HFP nanocomposite coating on glass by electrospinning, *Journal of Materials Chemistry*, 22 (2012) 18479-18485.
- [24] B.S. Lalia, E. Guillen-Burrieza, H.A. Arafat, R. Hashaikeh, Fabrication and characterization of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) electrospun membranes for direct contact membrane distillation, *Journal of Membrane Science*, 428 (2013) 104-115.
- [25] S. Kaur, R. Barhate, S. Sundarrajan, T. Matsuura, S. Ramakrishna, Hot pressing of electrospun membrane composite and its influence on separation performance on thin film composite nanofiltration membrane, *Desalination*, 279 (2011) 201-209.

502 [26] M. Khayet, T. Matsuura, MD Membrane Characterization, (2011) 189-225.

503 [27] D. Li, Y. Xia, Electrospinning of nanofibers: reinventing the wheel?, Advanced materials,
504 16 (2004) 1151-1170.

505 [28] J.R.K. Sung Won Choi, Young Rack Ahn, Seong Mu Jo, and, E.J. Cairns, Characterization
506 of Electrospun PVdF Fiber-Based Polymer Electrolytes, Chem. Mater., 19 (2007) 104 - 115.

507 [29] E.N. Dalal, Calculation of solid surface tensions, Langmuir, 3 (1987) 1009-1015.

508 [30] F.A. Dullien, Porous media: fluid transport and pore structure, Academic press, 2012.

509 [31] F.C. Krebs, Fabrication and processing of polymer solar cells: a review of printing and
510 coating techniques, Solar Energy Materials and Solar Cells, 93 (2009) 394-412.

511 [32] M. Buonomenna, P. Macchi, M. Davoli, E. Drioli, Poly (vinylidene fluoride) membranes by
512 phase inversion: the role the casting and coagulation conditions play in their morphology,
513 crystalline structure and properties, European Polymer Journal, 43 (2007) 1557-1572.

514 [33] C.M. Hansen, Hansen solubility parameters: a user's handbook, CRC press, 2007.

515 [34] S. Nejati, C. Boo, C.O. Osuji, M. Elimelech, Engineering flat sheet microporous PVDF
516 films for membrane distillation, Journal of Membrane Science, 492 (2015) 355-363.

517 [35] D. Blundell, A. Keller, A. Kovacs, A new self- nucleation phenomenon and its application
518 to the growing of polymer crystals from solution, Journal of Polymer Science Part B: Polymer
519 Letters, 4 (1966) 481-486.

520 [36] A. Ahmad, N. Ideris, B. Ooi, S. Low, A. Ismail, Morphology and polymorph study of a
521 polyvinylidene fluoride (PVDF) membrane for protein binding: Effect of the dissolving
522 temperature, Desalination, 278 (2011) 318-324.

523 [37] M. Tomaszewska, Preparation and properties of flat-sheet membranes from poly (vinylidene
524 fluoride) for membrane distillation, Desalination, 104 (1996) 1-11.

525 [38] P. Sukitpaneenit, T.-S. Chung, Molecular elucidation of morphology and mechanical
526 properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and
527 rheology, Journal of Membrane Science, 340 (2009) 192-205.

528 [39] W. Pu, X. He, L. Wang, C. Jiang, C. Wan, Preparation of PVDF–HFP microporous
529 membrane for Li-ion batteries by phase inversion, Journal of membrane science, 272 (2006) 11-
530 14.

531 [40] C.-Y. Kuo, H.-N. Lin, H.-A. Tsai, D.-M. Wang, J.-Y. Lai, Fabrication of a high
532 hydrophobic PVDF membrane via nonsolvent induced phase separation, Desalination, 233 (2008)
533 40-47.

534 [41] L.-Y. Yu, Z.-L. Xu, H.-M. Shen, H. Yang, Preparation and characterization of PVDF–SiO₂
535 composite hollow fiber UF membrane by sol–gel method, Journal of Membrane Science, 337
536 (2009) 257-265.

537 [42] J.F. Li, Z.L. Xu, H. Yang, C.P. Feng, J.H. Shi, Hydrophilic microporous PES membranes
538 prepared by PES/PEG/DMAc casting solutions, Journal of applied polymer science, 107 (2008)
539 4100-4108.

- [43] C. Yao, X. Li, K. Neoh, Z. Shi, E. Kang, Antibacterial activities of surface modified electrospun poly (vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP) fibrous membranes, *Applied Surface Science*, 255 (2009) 3854-3858.
- [44] A. Tuteja, W. Choi, M. Ma, J.M. Mabry, S.A. Mazzella, G.C. Rutledge, G.H. McKinley, R.E. Cohen, Designing superoleophobic surfaces, *Science*, 318 (2007) 1618-1622.
- [45] M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces, *Langmuir*, 16 (2000) 5754-5760.
- [46] A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, Preparation of transparent superhydrophobic boehmite and silica films by sublimation of aluminum acetylacetonate, *Advanced Materials*, 11 (1999) 1365-1368.
- [47] S. Srinivasan, G.H. McKinley, R.E. Cohen, Assessing the accuracy of contact angle measurements for sessile drops on liquid-repellent surfaces, *Langmuir*, 27 (2011) 13582-13589.
- [48] K. Smolders, A. Franken, Terminology for membrane distillation, *Desalination*, 72 (1989) 249-262.
- [49] A. Wessel, On using the effective contact angle and the water drop penetration time for classification of water repellency in dune soils, *Earth Surface Processes and Landforms*, 13 (1988) 555-561.
- [50] M.C. Garcia-Payo, M.A. Izquierdo-Gil, C. Fernandez-Pineda, Wetting Study of Hydrophobic Membranes via Liquid Entry Pressure Measurements with Aqueous Alcohol Solutions, *J Colloid Interface Sci*, 230 (2000) 420-431.
- [51] D. Murakami, H. Jinnai, A. Takahara, Wetting transition from the Cassie–Baxter state to the Wenzel state on textured polymer surfaces, *Langmuir*, 30 (2014) 2061-2067.
- [52] C. Huh, S. Mason, Effects of surface roughness on wetting (theoretical), *Journal of colloid and interface science*, 60 (1977) 11-38.
- [53] M. Gryta, Effectiveness of water desalination by membrane distillation process, *Membranes*, 2 (2012) 415-429.