Structural tailoring of hierarchical fibrous composite membranes to balance mass transfer and heat transfer for state-of-the-art desalination performance in membrane distillation†

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Membrane distillation (MD) displays superior characteristics to other technologies to alleviate the ever-increasing freshwater crisis through seawater desalination and/or wastewater recycling. However, the critical challenge in MD is fabricating high-performance membranes. In this study, we fabricated a high-performance hierarchical fibrous composite (HFC) membrane to acquire a high water flux while maintaining a high salt rejection for MD. This HFC membrane comprises of a thin active dense layer with small poly(vinylidene fluoride-co-hexafluoropropylene) (PH) nanofibers to allow maximum mass transfer and a thick support layer with large polyethylene terephthalate (PET) microfibers to give minimum heat transfer. By tailoring the structures of both the active and support layers to reduce the trade-off between the mass transfer and heat transfer during the MD process, the optimized HFC membrane, having a 3 μm thick PH active layer and 70 μm thick PET support layer, achieved the highest reported water flux of 79.21 ± 4.17 L m⁻² h⁻¹ and the salt rejection was higher than 99.9% using 3.5 wt% NaCl as the feed under a temperature difference of 40 °C in direct contact membrane distillation (DCMD). Our study describes a novel HFC membrane which demonstrates great achievements in elevating the MD performance.

Introduction

Population growth and environmental pollution, accompanied by industrial development, means that freshwater shortage is becoming an unprecedented crisis which is attracting ever-increasing attention from researchers. ¹,² Seawater desalination and wastewater reuse have evolved into the most effective strategies to alleviate this crisis.³ The predominant technologies are membrane (e.g., reverse osmosis, RO) and thermal (e.g., multi-effect distillation, MED) based methods.⁴ Nevertheless, these two technologies are challenged by high energy consumption in terms of either the high operating pressures or the large consumption of high temperature steam. Membrane distillation (MD) is a method that emerged in the 1960s⁵ and has attracted tremendous attention owing to its superiority to traditional methods.⁶ MD is a hybrid thermal/membrane process driven by the vapor pressure gradient, during which mass transfer in the vapor phase occurs through the hydrophobic membrane from the hot side (320–350 K) and condenses in the cold side.⁷ Compared to RO and MED, MD exhibits several advantages such as high production quality, the ability to use low-grade waste heat, high energy-efficiency, independence of the feed solution salinity, and so forth.⁸ Hence, MD plays an important role in acquiring clean water through desalination and/or wastewater recycling.⁹

Traditional MD membranes are derived from currently used hydrophobic ultrafiltration membranes such as polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE), and fabricated via phase inversion, stretching, and so forth.¹⁰ The main limitation of these membranes is their...
low permeability owing to the low porosity. Hence, efforts have been made to improve the water flux of MD through membrane design, configuration optimization, and process design.\textsuperscript{11–13} In particular, the design and development of membranes with a high porosity to enhance the water flux has been investigated, among which electro-spun nanofibrous membranes (ENMs) have been proven to be an ideal alternative.\textsuperscript{14} ENMs present great advantages (e.g., high hydrophobicity, high porosity, low tortuosity, tunable pore size, narrow pore size distribution, customizable structure, availability of more candidate materials, and scalability) when being used as MD membranes. Permeability can be significantly enhanced by using ENMs to replace the flat-sheet or hollow fibrous membranes made using other methods. For all of the derived PVDF membranes, ENMs achieved a much higher water contact angle (WCA, 138°) and a higher water flux (21.4 L m\textsuperscript{-2} h\textsuperscript{-1}, LMH) than those obtained for flat (83°, 13.6 LMH) and hollow fibrous membranes (105°, 11.5 LMH).\textsuperscript{15–17} Ongoing research has further enhanced the permeability of ENMs in MD. Novel ENMs, represented by poly(vinylidene fluoride-co-hexafluoropropylene) (PH) exhibited a much higher water flux of 30–40 LMH compared to those of commercial membranes which had a water flux of 20–25 LMH under the same experimental conditions.\textsuperscript{18–20} In addition, diverse strategies including surface modifications \textit{via} fluorine containing agents\textsuperscript{19,21–23} and inorganic nanoparticles (TiO\textsubscript{2},\textsuperscript{22,23} SiO\textsubscript{2},\textsuperscript{24,25} CNTs,\textsuperscript{26–28} etc.) can be used to functionalize the ENMs and acquire superhydrophobic surfaces with a contact angle (CA) of more than 150°.

In spite of the aforementioned advances, optimizing the performance of MD membrane by structures design has not received significant research attention, but might have an unexpected effect. It was reported that permeability could be enhanced by dual-layer ENMs design in MD.\textsuperscript{29–31} For instance, the dual-layer ENMs of PVDF/PSf exhibited about 40% higher water flux than that of the single PVDF ENMs,\textsuperscript{32} which benefited from a more open structure of the polysulfone layer with a large fiber diameter used as a support to reduce the mass transfer resistance and also minimize the heat transfer, compared with a single layer of dense and thick PVDF ENMs. A significant enhancement in the permeability of the ENMs would be expected if the top layer was dense and thin enough to prevent wetting and to reduce the mass transfer resistance, and if the support layer was open and thick to prevent temperature polarization and to reduce the mass transfer resistance. This inspires us to design a more ideal and promising hierarchical fibrous membrane based on dual layer ENMs to further advance the performance of the MD membranes, learning from the concept of the thin-film composite (TFC) membrane. A TFC membrane is a kind of composite membrane comprising of an ultrathin active layer and a thick support layer, which works as a state-of-the-art membrane structure for desalination\textsuperscript{34} and air filtration.\textsuperscript{35,36} these membranes feature a high permeability which is attributed to the ultrathin selective layer of the TFC structures. However, such membranes have not yet been applied in MD, which could be very promising and would hopeful improve the vapor permeations. In MD, the membrane water flux can be optimized through balancing the mass transfer and the heat transfer. For the hierarchical fibrous composite (HFC) membrane, the thin active layer with a small fiber diameter, small pore size, and very thin thickness provides a reduced mass transfer resistance and can achieve high permeations with high salt rejections, but also high heat loss. The thick support layer with a large fiber diameter, large pore size, low tortuosity, high porosity and high mechanical strength could significantly decrease the mass transfer resistance, but also increase the heat transfer hindrance. The synergistic effect of the active and support layer endows the HFC membrane with a high permeability and high salt rejections by maximizing the mass transfer and minimizing the heat transfer during the MD process.

Herein, we fabricated hierarchical fibrous composite (HFC) membranes for membrane distillation. The HFC membrane comprises of a thin active dense layer with small PH nanofibers and a thick support layer with large PET microfibers (Scheme 1). The thin active layer of PH nanofibers with small pores is used to increase mass transfer with anti-wetting properties in the MD process, and the thick support layer of PET microfibers with large pores is used to prevent heat transfer and also increase mass transfer. Electro-spinning was employed to fabricate the PH nanofibers on top of the electro-spun PET microfibers. The HFC membrane structure was tailored by tuning the thickness of each layer and also the fiber diameters \textit{via} adjustment of the electrospinning parameters, and the interplay of the active and support layer was also systematically investigated. Importantly, the transport properties of the HFC membranes, including the water flux and salt rejection was measured in the direct contact membrane distillation (DCMD) process. The structure-properties of the HFC membrane were also investigated to identify the impact of each PH and PET individual layer on the performance in the MD process. We also elucidated the ideal structure for high-performance electro-spun fibrous membranes for MD and identified the impact of the membrane structure on the mass transfer and heat transfer of the MD process.

Materials and methods

Materials and chemicals

Polyethylene terephthalate (M\textsubscript{w}: 30–80 kDa) was obtained from recycled Coca Cola bottles (99.8 wt% purity without plasticizers,
Coca-Cola Enterprise, China). All bottles were cleaned with water and ethanol sequentially, then dried at room temperature and cut into pieces. PH (Mw: 455 000 kDa) was purchased from Sigma Aldrich (St. Louis, MO, USA). Trifluoroacetic acid (TFA), acetone, N,N-dimethylacetamide (DMAC), isopropanol and n-hexane were supplied as analytical grade (AR) solvents from Shanghai Sinopharm Chemical reagent CO., LTD (China). Deionized (DI) water was obtained from Wahaha group CO., LTD (China).

**Fabrication of electrospun HFC membrane**

A series of PET solutions were prepared by dissolving PET pieces in TFA at varying concentrations of 15%, 20%, and 30% (w/v) (simplified as PET-1, PET-2 and PET-3, respectively). PVDF–HFP (simplified as PH) solution was prepared by dissolving PH in a mixture solution of DMAC and acetone (30/70, w/w) with concentration of 10% (w/v). All polymer solutions were stirred for 4 h to ensure complete dissolution and then degassed overnight at room temperature. A custom-made electrospinning device was used to fabricate polymeric fibers (Fig. S1†) and an alumina-covered copper plate was used as a collecting device.

HFC membranes were prepared by electro-spinning of PH nanofibers on top of the electro-spin PET microfibers. PET fibers were electro-spin first at a flow rate of 1.5 mL h⁻¹ under a voltage of 11.00–18.00 kV, followed by the electro-spinning PH nanofibers on top of PET fibers at a flow rate of 1.0 mL h⁻¹ under a voltage of 22.00 kV. The collecting distance between the spinneret and the collecting copper plate was 12 cm. The diameter of the PET microfibers was tailored by varying the concentration of the PET solution, and the thicknesses of PET microfibers and PH nanofibers were controlled by tuning the volume of the electrospun polymer solutions. The entire electrospinning process was performed in a controllable environmental chamber at a fixed temperature of 25 °C and a relative humidity of 35 RH%. The heatpressing treatment was performed under a pressure of 0.7 kPa at 130 °C for 30 min, then in a mixture of isopropanol and DI water (1:1, vol:vol) for 30 min, and then DI water for at least 8 h in sequence to ensure complete wetting, the fully wetted membrane coupons were weighed at room temperature after wiping the superficial water off the membrane coupon surfaces. The porosity was calculated using eqn (1):  

\[
e = \frac{(m_2 - m_1)/\rho_i}{(m_2 - m_1)/\rho_i + m_1/\rho_p}
\]  
in which \( m_i \) is the weight of the dry membrane (g), \( m_2 \) is the weight of the wet membrane (g), \( \rho_i \) is the water density (1.00 g mL⁻¹), and \( \rho_p \) is the polymer density (1.68 g mL⁻¹ for PET and 1.77 g mL⁻¹ for PH). At least three individual samples were measured in parallel experiments.

The LEPW (liquid entry pressure of water, kPa) of the electro-spin fibrous membranes was tested using homemade equipment (Fig. S2†) following the reported protocol. The dry membrane samples (with a diameter of 3 cm) were placed into the membrane cell and the reservoir was filled with DI water. The air pressure was increased at the rate of 0.5 kPa min⁻¹ and each pressure was maintained for 10 min during the process of the LEPW test. The minimum pressure resulting in the first water drop across the membrane was the LEPW value.

The thermal conductivity coefficients of the membranes were measured using a HotDisk thermal constants analyzer (TPS 2500S, HotDisk, Sweden). The HotDisk method requires no special sample preparation. The sample is simply placed between the two sensors of the thin film module.

**Membrane performance test**

A laboratory-scale DCMD system (shown in Fig. S3†) was equipped with a flat-sheet membrane cell having an 8 cm² effective area to determine the water flux and salt rejection of the fabricated membranes. Both the cold side (DI water, conductivity below 5.0 µs cm⁻¹) and hot side (3.5 wt% NaCl aqueous solution) solutions were circulated at a flow rate of 0.4 L min⁻¹ using a gear pump (WT3000-1FA, Longer Pump, China). The cold side was maintained at 25 ± 1 °C using a chiller (SDC-6, Ningbo Scientz Biotechnology CO., LTD, China), and the hot side was heated at 65 ± 1 °C using a heating bath (B-260, Shyaron Biochemical Instrument Factory, China). All of the tubes in the hot side were insulated to alleviate heat loss.
The effect of the operating parameters including the flow rate and temperature difference of the DCMD system were also investigated. The flow rate was set as 0.3, 0.4, and 0.5 L min⁻¹, respectively. The temperature of hot side was set to be 35, 45, 55, 65, 75 and 85 °C, respectively, while, the cold side was maintained at 25 °C.

The water flux of the fabricated membranes was monitored as the weight gain in the cold side at a fixed time interval, which was recorded using an electronic balance (ME3002, Mettler, Switzerland). The conductivity of the cold side (to calculate the NaCl concentration) was measured using a conductivity meter (CON2700, Eutech, USA). The salt (NaCl) rejection, \( R \), was calculated using the previously reported eqn (2),

\[
R = \left(1 - \frac{V_pC_p/J_wA_wt}{C_i}\right) \times 100\%
\]

in which \( V_p \) is the permeate water volume in the cold side (L), \( C_i \) is the initial NaCl concentration in the hot side (3.5 wt%), \( A_w \) is the effective membrane area (m²), and \( t \) is the time of the test (h).

Membrane stability test

The chemical and thermal stability of the fabricated membranes were evaluated in challenging conditions upon various treatments including acidic conditions (dilute HCl solution, pH: 1.42) and basic conditions (dilute NaOH solution, pH: 10.52) at room temperature for 6 h, and sonication at 65 °C for 2 h, respectively. The water contact angles of the top and bottom membrane surfaces were then measured at room temperature following the above described procedure.

Results and discussion

Properties of the active and support layer of the HFC membranes

Hierarchical fibrous composite membranes were fabricated through electro-spinning of a thin active layer of PH nanofibers on top of the thick support layer of PET microfibers. The membrane structure and surface properties including the surface morphology and hydrophobicity, fiber diameters, pore size, porosity, and liquid entry pressure (LEP) were comprehensively characterized as being critical membrane structure parameters. These properties of the PH and PET fibrous membranes were respectively investigated with each layer thickness (Fig. 1). All of the PH and PET fibrous membranes display a well-defined, consecutive, interconnected fibrous structure (Fig. 1a–d) with good hydrophobicity and having high WCs of 135–145°. However, the PH and PET layers exhibit distinctive differences in the fiber diameters and pore structures. The PH layer had a very fine fibrous morphology with a fiber diameter of 100 ± 61 nm (Fig. 1a). Comparatively, the PET layer (PET1, PET2, PET3) has much larger fiber diameters from 400 ± 107 to 1219 ± 206 nm, which were electro-spun using increasing solution concentrations from 15% to 30% respectively (Fig. 1b–d) and were tailored through the increased resistance from the electric stretching induced by the increased viscosity and decreased surface tension of the high concentration polymeric solution. The pore size of the PH nanofibrous membrane is 0.60 μm with a narrow pore size distribution owing to its small fiber diameter, while, that of PET-1, PET-2, PET-3 microfibrous membranes is 1.58, 3.03, and 10.02 μm respectively with a wide pore size distribution, increasing with their fiber diameters. The porosity of both the PH and PET membranes are in the range of 80–90%, high porosity is an advantage for fibrous membranes used as MD membranes.

The LEP is a key parameter that illustrates the anti-wetting properties of the MD membrane, and the lower the LEP, the stronger wetting propensity. The LEP of each layer of the PH and PET fibrous membranes was measured and there was an obvious increase with the membrane thickness (Fig. 1e and f). When the PH fibrous membrane is less than 1 μm thick, the LEPₚ was too low to be detected. When the thickness was 70 μm, the LEP of the PH fibrous membrane was 25.6 ± 4.3 kPa, which is 2–7 fold higher than that with the thickness of 3 and 6 μm. The same trend for the LEP was observed for the PET fibrous membranes. Notably, the PH fibrous membrane had a much higher LEP (~25 kPa) than the PET fibrous membrane (~8 kPa) with the same thickness of 70 μm owing to their different pore sizes. Additionally, the LEPₚ of the PET-3 membrane was barely detectable owing to its large pore size, even when the thickness was increased to 90 μm.

In order to optimize membrane structure, we first evaluated the impact of the membrane thickness on the water flux of individual PH and PET electro-spun fibrous membranes in the DCMD process (Fig. 2). All of the membranes achieve high salt rejections of more than 99.9% to produce high quality fresh water. Nevertheless, the membrane thickness imparts both mass and heat transfer resistances which affect the water flux of

| Sample | Thickness of PH active layer (μm) | Thickness of PET support layer (μm) | Fiber diameter of PET support layer (nm) | Liquid entry pressure (kPa) |
|--------|----------------------------------|-----------------------------------|----------------------------------------|---------------------------|
| D1     | 3 ± 1                            | 70 ± 5                            | 400                                    | 15.6 ± 4.8                |
| D2     | 3 ± 1                            | 70 ± 5                            | 788                                    | 13.4 ± 2.5                |
| D3     | 3 ± 1                            | 70 ± 5                            | 1219                                   | 5.3 ± 2.4                 |
| D4     | <1                               | 70 ± 5                            | 788                                    | 3.0 ± 0.8                 |
| D5     | 3 ± 1                            | 70 ± 5                            | 788                                    | 13.4 ± 2.5                |
| D6     | 6 ± 1                            | 70 ± 5                            | 788                                    | 14.6 ± 2.8                |
| D7     | 3 ± 1                            | 50 ± 5                            | 788                                    | 6.4 ± 4.8                 |
| D8     | 3 ± 1                            | 70 ± 5                            | 788                                    | 13.4 ± 2.5                |
| D9     | 3 ± 1                            | 90 ± 5                            | 788                                    | 15.3 ± 3.3                |
both the PH (Fig. 2a) and PET (Fig. 2b) membranes. As the thickness of the PH electro-spun fibrous membrane increased from 3 to 6 μm, the membrane water flux increased from 27.35 ± 2.95 to 34.01 ± 3.13 LMH. A further thickness increase to 70 μm significantly decreased the water flux rapidly to 15.45 ± 2.91 LMH. This change is expected to be the competitive balance of the increased mass and heat transfer resistance from the membrane thickness increase in MD. For an ideal MD membrane, the resistance to mass transfer should be as low as possible for a high permeation and a high flux while that for heat transfer should be as high as possible for the prevention of heat loss and temperature polarization (TP) to maintain a high vapor pressure difference as a driving force. The increase in the water flux for the PH membrane from 3 to 6 μm thick is ascribed to the greater impact of the increased heat transfer resistance to suppress the temperature polarization across the membrane and achieve a higher driving force than the increased mass transfer resistance. Increasing the thickness to 70 μm tremendously increased the mass transfer resistance, leading to a sharp decrease in the water flux. Additionally, a very thin PH membrane that was 1 μm thick suffered from wetting issues and was unable to be used in MD. Similarly, the 50 μm thick PET membrane also failed to be tested owing to a rapid wetting problem in MD. With the increase in the thickness of the PET membrane from 70 to 90 μm, the water flux decreased from 29.94 ± 4.24 to 25.54 ± 3.09 LMH, which is mainly attributed to the increased mass transfer resistance.

The thin PH layer has a suitable LEP even with a thickness of less than 10 μm, although the PET layer needs to be very thick (70 and 90 μm). Notably, the LEP and water flux of the PH layer are susceptible to the thickness. A slight change in the thickness can induce a large fluctuation. However, the effect of the thickness of PET is comparatively very small. This unique characteristic is in good accordance with the concept of TFC membranes. The active layer with a dense structure plays a major role in salt rejections and the support layer with a loose structure acts as a heat proof support with enough mechanical strength. Thus, we constructed the HFC membrane with PH nanofibers as an active layer and PET microfibers as a support layer. The MD performance could be tuned by controlling the

![Fig. 1](image1.png) SEM micrographs of PH (a) and PET electrospun fibers using different PET concentrations of 15%, PET-1 (b), 20%, PET-2 (c) and 30%, PET-3 (d) respectively. LEP<sub>w</sub> of PH electrospun membranes with different thicknesses (e), and PET electrospun membranes with different fiber diameters and thicknesses (f). Characteristic parameters of PH and PET electrospun membranes are shown in the table, including the thickness, fiber diameter, water contact angle, pore size and porosity.

![Fig. 2](image2.png) Impact of the membrane thickness on the water flux of the individual PH (a) and PET (b) fibrous membranes in the DCMD process (operation conditions: feed solution, 3.5 wt% NaCl, 65 °C; permeate, DI water, 25 °C; velocity: 0.4 L min<sup>-1</sup>).
mass and heat transfer via optimization of both the PH and PET layers.

**Structure optimization of HFC membranes**

High-flux MD membrane should be as thin as possible to decrease the mass transfer resistance. Nevertheless, the thinner the membrane thickness is, the more severe the heat loss and the temperature polarization across the membrane, and thus the smaller the driving force of MD. Therefore, the optimal HFC membrane structure has a thickness that can balance the heat transfer and mass transfer resistance in MD. The structure optimization of the HFC membrane could completely eliminate this trade-off. The very thin PH layer should decrease the mass transfer resistance to a minimum, meanwhile, the thick and loose PET layer should decrease the heat transfer to the minimum with very little effect on the extra mass transfer resistance owing to the large pore size and loose structure. The synergistic effect of the PH and PET layers endows the HFC membrane with the expected excellent MD performance. We systematically investigated and optimized the HFC membrane structures by tailoring the PH (thickness) and PET layer (thickness and fiber diameters) to maximize their MD performance (Fig. 3a and b).

Firstly, we investigated the influence of the fiber diameters of the PET layer on the MD performance of the HFC membrane (Fig. 3c). The thickness of the PH and PET layer were fixed as 3 and 70 μm, respectively. The diameter of the PH layer was also fixed at 100 nm, while those of the PET layer were 400, 788, and 1219 nm. All of the membranes achieve high salt rejections of greater than 99.9%. By increasing the fiber diameter of PET from 400 (D1) to 788 (D2) nm, the water flux of the HFC membrane significantly increased from 35.56 ± 2.41 to 79.21 ± 4.17 LMH. A further increase of the PET fiber diameter to 1219 nm (D3) leads to a sharp decrease in the water flux of the HFC membrane to 42.65 ± 6.78 LMH. This is a competitive result for the mass transfer, heat transfer, and anti-wetting properties (Fig. 3d). With an increase in the fiber diameter, the increased pore size indicates a decreased mass transfer resistance. Both the LEPw and the thermal conductivity coefficient decrease with increasing fiber diameters, indicating the decreased heat transfer and wetting tendency. The water flux increase of the HFC membrane from D1 to D2 is ascribed to the greater effect of the increased mass transfer compared to that of the increased heat transfer and wetting. However, the heat transfer and wetting tendency increased so dramatically that even with the further decreased mass transfer, the water flux of the HFC membrane at D3 is still significantly decreased.

We further optimized the structures and MD performance of the HFC membranes by altering the thickness of the PH (Fig. 4a) and PET (Fig. 4b) individual layers. All of the membranes had high salt rejections of more than 99.9%. When the PH layer thickness is less than 1 μm, severe wetting was observed with a sharp decrease in the water flux within approximately 15 min and gradually decreased salt rejections (Fig. S4†). With a PH layer of 3 μm, the membrane exhibits a stable water flux of 79.21 ± 4.17 LMH. Increasing the PH thickness to 6 μm leads to a significant reduction in the water flux to 32.04 ± 1.20 LMH, which is ascribed to the significantly enhanced mass transfer resistance, in spite of the slightly reduced heat transfer (Fig. 4c). Decreasing the PET support layer thickness from 70 to 50 μm reduces the water flux from 79.21 ± 4.17 to 30.02 ± 1.33 LMH, which is mainly attributed to the wetting owing to the thin PET layer with a low LEPw, accompanied by the increased heat
transfer (Fig. 4d). Increasing the PET thickness from 70 to 90 µm sharply reduces the water flux from 79.21 ± 4.17 to 16.35 ± 1.93 LMH, which could be due to the significantly enhanced mass transfer resistance.

By tailoring the structure, we can confirm the best optimization of the thus fabricated HFC membrane. The membrane comprised of a PH active layer with a thickness of 3 µm and a diameter of 100 nm and a PET support layer with a thickness of 70 µm and a diameter of 788 nm displays the maximum MD performance. By using 3.5 wt% NaCl as the feed solution and with a temperature difference of 40 °C, the water flux of the optimized HFC membrane can be as high as 79.21 LMH with a salt rejection of more than 99.9%, which is 2–3 times higher than that of the PH (27.35 ± 2.95 LMH) and PET (29.94 ± 4.34 LMH) individual layers with comparably high salt rejections. We compared the DCMD performance of our fabricated HFC membranes with other reported fibrous membranes under the same measuring conditions (3.5 wt% NaCl as feed, DI water as the permeate, a temperature difference is 40 °C) (Fig. 5b). As the salt rejections are all very high (>99%) for DCMD, we only compared the water flux. Obviously, our membrane exhibits distinct advantages over the other fibrous membranes. Even compared with the highest reported water flux (42 LMH),24 our membrane still displays a prominent superiority. Therefore, it can be supposed that the strategy we proposed here could have great potential to take a big step on the road of pushing forward the exploration of more advanced MD membranes.

Effect of operating parameters on DCMD

The operating parameters that influence the MD performance (mainly water flux) include the temperature difference, feed salinity, feed and permeate flow rate. The temperature difference acts as an original driving force and has the most prominent effect.23 The effect of the feed salinity has little effect on the water flux.24 For the flow rate, it is easy to understand that increasing either the feed side or permeate flow rate could favor maintaining of the thermal driving force and thereby the high water flux. Thus, we further investigated the impact of the temperature difference and flow velocity on the MD performance of the HFC membranes to evaluate the elevating space (Fig. 6). It is worth mentioning that all of the membranes held very high salt rejections of more than 99.9% under the tested conditions. Fig. 6a shows that the water flux of the HFC membrane increases with the temperature difference between the feed and permeate side. By increasing the temperature difference to 60 °C, the water flux of the HFC membrane can reach as high as 90 LMH (Fig. 6a), which is the currently reported ultra-high flux for DCMD. The effect of the flow rate is comparatively smaller. As the flow rate increases from 0.2 to 0.6 L min⁻¹, the water flux of the HFC membrane gradually increases from 56.50 to 70.09 LMH (Fig. 6b).

Stability of the HFC membranes

We further investigated the stability of the HFC membranes (Fig. S5†). Firstly, we evaluated the long-term performance of the optimized HFC membrane in the MD process (Fig. S5a†). Within the testing period of more than 100 h, the membrane water flux remained at the level of the initial value in spite of small fluctuations owing to fluctuations from the temperature controllers, and the salt rejection remained higher than 99.82%, with a very slightly decline. Thus, the fabricated HFC membrane exhibits good long-term stability. Furthermore, we also investigated the stability of the HFC membranes after treatment under various harsh conditions including 1 h sonication, and immersion for 1 h in acid (pH = 2.45) and alkaline (pH = 10.35) conditions. The results shown in Fig. S5b† demonstrate that the membrane flux or salt rejection did not change significantly under these harsh treatments, suggesting that the HFC membrane is very stable under various harsh conditions.

Conclusions

We have reported the development of a novel kind of HFC membrane which displays a state-of-the-art performance in the DCMD system. The HFC membrane comprises both an active and support layer, which play different roles to balance the mass transfer and heat transfer. The thin PH nanofibrous layer with smaller fiber diameters, a smaller pore size, and narrower pore size distribution act as an active layer to provide a high salt rejection and anti-wetting properties. In addition, the active layer is very thin (the thickness is only 3 µm) and can decrease the mass transfer resistance as far as possible. The thick PET
microfibrous layer with larger fiber diameters, a larger pore size, and higher mechanical strength act as a support layer to decrease the heat transfer while having little effect on the mass transfer. The synergetic effect of the PH active layer and the PET support layer endows the HFC membrane with an excellent DCMD performance with the highest reported water flux of $79.21 \pm 4.17 \text{LMH}$ and a salt rejection of more than 99.9% using 3.5 wt% NaCl as a feed and DI as a permeate under a temperature difference of $40 \, ^\circ \text{C}$. Moreover, the HFC membrane exhibits good long-term stability and also maintains a great hydrophobic surface even after harsh treatments including sonication, and acid and basic challenging conditions. Our study stems from structure design that is based on the fundamental theory of MD and may offer a versatile strategy to construct a HFC membrane with a more advanced MD performance.

Conflicts of interest

The authors declare no competing financial interests.

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