Preparation of PVDF-CTFE hydrophobic membranes for MD application: Effect of LiCl-based mixed additives

Libing Zheng^{a,b}, Zhenjun Wu^c, Yuansong Wei^{a,b}, Yong Zhang^{a,b}, Yue Yuan^{a,b}, Jun Wang^{a,b,*}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

^b Beijing Key Laboratory of Industrial Wastewater Treatment and Resource Recovery, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^c College of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form

14 January 2016

Accepted 23 January 2016

Available online 27 January 2016

Keywords:

PVDF-CTFE

Mixed additives

LiCl

PEG

Membrane distillation

ABSTRACT

Hydrophobic flat-sheet membranes were prepared by poly (vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) via the non-solvent induced phase separation (NIPS) process for membrane distillation (MD) application. Different types of LiCl-based mixed additives were applied to investigate their effects on membrane properties and MD performance. The membranes were evaluated in terms of membrane morphology, pore size and distribution, porosity, surface roughness, hydrophobicity, as well as the direct contact membrane distillation (DCMD) performance. Clear evidences were obtained that the mixed additives altered the phase inversion process, which resulted in the variation in membrane morphology, structure, properties and performance. The mass ratio of PEG/LiCl ranging from 5:0 to 0:5 was comprehensively investigated to study the synergistic effects of two additives on PVDF-CTFE membranes. The membrane M5 (PEG:LiCl = 1:1, total content 8 wt%) showed optimal properties and MD performance for combining the structure of higher hydrophobicity and pore interconnectivity, small pore size and narrow pore size distribution. The addition of LiCl to PEG-containing solutions benefited the solid-liquid demixing process, which increased the hydrophobicity, porosity, pore interconnectivity, and MD performance of the resultant membranes. While added PEG to LiCl-containing solutions showed slightly influences. Furthermore, it was also found that PVP/LiCl and glycerol/LiCl were not suitable for hydrophobic membrane preparation as they strikingly reduced membrane hydrophobicity. While H₃PO₄ and H₂O were confirmed suitable to mix with LiCl for hydrophobic PVDF-CTFE membrane preparation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Hydrophobic membrane preparation and application have been a recent trend in membrane science to meet the demand of the hydrophobic membrane-based processes such as membrane distillation (MD) [1–3], membrane emulsification (ME) [4,5], supported liquid membrane (SLM) [6], osmotic distillation (OD) [7] and membrane crystallization (MCR) [8]. Most of the aforementioned processes are thermally-driven processes induced by the temperature difference, where the membranes functioned as a barrier and offered a liquid–vapor interface. The hydrophobicity of the membrane is crucial for these applications in order to prevent liquid phase from permeating through it. Membranes with poor hydrophobicity might induce the undesired pore-wetting issue which not only lowers the rejection rate but also reduces the long-term performance sustainability and operation life [9]. Meanwhile, the membranes are required to present excellent pore structure, which offers abundant passages for vapor transmission and

Abbreviations: ATRP, atom transfer radical polymerization; AFM, atomic force microscope; DMAc, N,N-dimethylacetamide; DCMD, direct contact membrane distillation; DMAc, dimethylacetamide; FE-SEM, field emission scanning electron microscope; GS, gas separation; L–L, liquid–liquid; MF, microfiltration; ME, membrane emulsification; MCR, membrane crystallization; MD, membrane distillation; NIPS, non-solvent induced phase separation technique; NF, nanofiltration; OD, osmotic distillation; PVDF, polyvinylidene fluoride; PVDF-CTFE, polyvinylidene fluoride-co-chlorotrifluoroethylene; PEGMA, poly (ethylene glycol) methyl ether methacrylate; PVDF-TFE, poly (vinylidene fluoride-trifluoroethylene); PVDF-HFP, poly (vinylidene fluoride-co-hexafluoropropylene); PVDF-TrFE, poly (vinylidene fluoride-trifluoroethylene); PVP, polyvinyl pyrrolidone; PEG, polyethylene glycol; PET, polyester; PE, polyethylene; PP, Polypropylene; PV, Pervaporation; RO, reverse osmosis; S–L, solid–liquid; SLM, supported liquid membrane; SEM, scanning electron microscope; UF, Ultrafiltration

* Corresponding author at: Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China.

E-mail address: junwang@rcees.ac.cn (J. Wang).

guarantees the membrane permeability. Thus, the hydrophobic membrane with appropriate chemical–physical properties, high hydrophobicity and permeability is the key point for further development of these hydrophobic membrane-based process, especially when speaking to the industrial application [10,11].

Fluoropolymers have been considered as the excellent candidate for hydrophobic membrane preparation due to the low surface tension derived from the low polarity and strong electro-negativity of the fluorine atom and the strong C–F bond ($485 \text{ kJ}\cdot\text{mol}^{-1}$) [12,13]. PVDF and PVDF-based copolymers such as poly (vinylidene fluoride-co-tetrafluoroethylene) (PVDF-TFE) [14,15], poly (vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) [16], and poly (vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) [17–19] were commonly used for hydrophobic membrane preparation for their excellent chemical and mechanical properties. PVDF-CTFE is another common PVDF-based copolymer [13,20] which has shown potentials in membrane preparation. Due to the incorporation of CTFE group, PVDF-CTFE is possible to be grafted via atom transfer radical polymerization (ATRP) in a mild condition without sacrificing the excellent mechanical, thermal, and chemical stabilities owing to the C–Cl bond. Kim et al. [21,22] synthesized a graft copolymer, i.e., PVDF-CTFE-g-PSSA via ATRP and applied it to electrolyte membranes and composite nanofiltration (NF) composite membrane preparation. It evidenced that these membranes presented good properties and performances during the lab-scale study. Meanwhile, poly (hydroxyl ethyl acrylate) [23], poly (oxyethylene methacrylate) [24], and 4-vinylpyridine [25] have also been grafting to the PVDF-CTFE to obtain the corresponding amphiphilic copolymer membranes. Liu et al. [26] had prepared PVDF-CTFE hydrophobic porous membranes by NIPS, and further hydrophilic modified with the immobilization of hydrophilic poly (ethylene glycol) methyl ether methacrylate (PEGMA) by ATRP for membrane filtration. To our best knowledge, although numerous efforts have been dedicated to applying PVDF-CTFE copolymer to membrane preparation, its potential in hydrophobic membrane preparation was overlooked. Thus, PVDF-CTFE copolymer was carefully compared with PVDF from physico-chemical property to phase diagram, as well as the hydrophobic membrane properties and DCMD performance in our previous work [27]. PVDF-CTFE showed excellent properties for hydrophobic membrane preparation and MD desalination application due to the ideal structure and DCMD performance. However, systematic study of PVDF-CTFE hydrophobic membrane preparation and modification is still required. So, one objective of this work is to investigate the preparation and tuning the PVDF-CTFE hydrophobic membranes by LiCl based mixed additives.

The addition of different types of additives was a key point in polymer membrane preparation by NIPS, which show significant influences on the membrane morphology, structure, properties, as well as the separation performance due to their effects on the phase inversion process [19,28]. However, the roles of different additives varied in diverse polymer/solvent/non-solvent systems. Meanwhile, mixed additives have been a recent trend for polymer membrane preparation due to the synergistic effect among different additives. Polyethylene glycol (PEG) is a commonly used pore-former for membrane preparation, and the PVDF membrane prepared with PEG normally possesses a macrovoid structure with high porosity owing to the instantaneous phase inversion process induced by PEG [29–33]. LiCl is another frequently-used additive, which tends to enhance the viscosity of the casting solution. Consequently, macrovoids were suppressed and the membrane with excellent interconnectivity and porosity can be gained, however at the expense of decline in mechanical strength [19,33,34]. As such, attempts were made to use PEG/LiCl mixed additives for membrane preparation in order to synergize the advantages of both additives [32,35,36]. Nonetheless, as a crucial

factor to membrane properties and performance, the PEG/LiCl mass ratio in casting solution has not been investigated systematically and its impacts on the resultant membranes have hardly been reported.

In the present contribution, PVDF-CTFE hydrophobic membranes were prepared using PEG/LiCl mixed additives and the of PEG/LiCl mass ratio was systematically investigated in terms of membrane pore size, porosity, and hydrophobicity, morphology, and MD performance. Other types of additives including polyvinyl-pyrrolidone (PVP), H_3PO_4 , glycerol, and H_2O were also mixed with LiCl and used as additives for membrane preparation. This work attribute to present a comprehensive understanding of PEG/LiCl mixed additives, and also provide a reference for other LiCl-based mixed additives.

2. Experimental

2.1. Materials

PVDF-CTFE powder (Solef® 32008, Solvay, Belgium) was desiccated at 50°C for 24 h before being used in casting solution preparation to removal residual moisture. DMAc (Tech, > 99.0%), purchased from Shanghai Jingwei Chemical Co., Ltd, was applied as solvent. LiCl (AR, > 97.0%) and PEG ($M_w=400$, AR), supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering, were applied as additives. PVP K60 (AR, > 95.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Glycerol (GR, > 99.0%), H_3PO_4 (GR, > 85.0%), Ethanol (GR, > 99.7%), NaCl (GR, > 99.8%), and diiodomethane (GR, > 98.0%) were offered by Sinopharm Chemical Reagent Co., Ltd. Tap water was used as non-solvent in the coagulation bath.

2.2. Casting solution preparation

A desired amount of solvent and additives were firstly mixed in a sealed flask and mechanically stirred at 30°C for at least 5 h to completely dissolve the additives. Then the pre-dried PVDF-CTFE powder was poured into the flask and continuously stirred to homogenize the solution for at least 24 h. Subsequently, the polymer solution was kept in a vacuum oven (30°C , 24 h) for vacuum-degassing. Thirteen casting solutions were prepared in this work, the detailed compositions were listed in Table 1.

2.3. Cloud point experiment

The cloud point of each casting solution was acquired using the

Table 1
Compositions of the polymer solutions for membrane casting.

Membrane code	PVDF-CTFE (wt.%)	Additives	Mixing ratio	Additives content (wt%)	DMAC content (wt%)
M1	12	PEG/LiCl	5:0	5	83
M2	12	PEG/LiCl	5:1	5/1	82
M3	12	PEG/LiCl	5:2	5/2	81
M4	12	PEG/LiCl	5:3	5/3	80
M5	12	PEG/LiCl	4:4	4/4	80
M6	12	PEG/LiCl	3:5	3/5	80
M7	12	PEG/LiCl	2:5	2/5	81
M8	12	PEG/LiCl	1:5	1/5	82
M9	12	PEG/LiCl	0:5	5	83
M10	12	LiCl/PVP	5:2	5/2	81
M11	12	LiCl/ H_3PO_4	5:2	5/2	81
M12	12	LiCl /Glycerol	5:2	5/2	81
M13	12	LiCl/ H_2O	5:2	5/2	81

titration method as described in the previous work [37]. The test was conducted at 30 °C in this work. The end point was recorded as the solutions became irreversibly turbid (solution with low viscosity) or showed irreversibly sign of gelation (solution with high viscosity) as detected visually. The phase diagram was plotted by the content of polymer, non-solvent, additives and solvent. It should make clear that the integration of additives and solvent were considered as one phase, and the sum of their contents was plotted in the phase diagram.

2.4. Membrane preparation

Before membrane casting, a piece of PET nonwoven fabric was attached to a clean flat glass plate. Then the degassed solution was casted in an oven (50 °C) with a home-made knife, the thickness of the flat spread solution was 250 μm. The as-prepared nascent membrane was immersed into the coagulation bath (25 °C, 24 h) after air exposure (15 s). The membrane was subsequently water-rinsed to further remove the residual solvent and additives. Finally, the wet membrane was dried in air and preserved in zip-lock bag for subsequent measurement and application.

2.5. Membrane characterization

A Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA) was used to investigate the effect of the additives on the chemical structure of PVDF-CTFE copolymer. The spectra were recorded in a wave number range of 4000–600 cm⁻¹ by cumulating 64 scans at a resolution of 2 cm⁻¹.

Field emission scanning electron microscope (FE-SEM) (HITACHI SU8020, Hitachi, Japan) was utilized for membrane surface and cross-sectional morphology observation. For cross-section observation, the membrane was firstly cryogenically fractured in liquid nitrogen. And then all the samples were gold nanoparticle-coated under vacuum condition (HITACHI E-1010, Hitachi, Japan) prior to SEM observation.

As SEM image was not enough for surface stereogram and roughness analysis, atomic force microscope (AFM) (Shimadzu SPM-9600, Shimadzu, Japan) was also employed. Tapping mode was used with the same probe at a scan size of 5.0 μm × 5.0 μm. The 3D surface morphology and depth distribution images were obtained, as well as the roughness data.

The membrane hydrophobicity was represented by the contact angles between membrane and three liquids with different polarity, i.e., deionized water, glycerol, and diiodomethane, by an OCA 15EC Video-Based Contact Angle Meter (Data Physics, Germany). Liquid droplets of about 0.5 μL were carefully dropped onto the upper surface of the flat-sheet membrane (PVDF-CTFE top side) with a syringe under ambient temperature, and the contact angles were obtained by measuring five different positions of each sample. The membrane surface free energy was calculated using the Owens method [38] as follows:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} \quad (1)$$

where, γ_S , γ_S^d , γ_S^p , γ_L , γ_L^d , γ_L^p represent the surface free energy, dispersion force term and polar force term of the solid and the liquid, which were presented in Table 2. Then γ_S^d , γ_S^p were calculated by Eq.(1) with the measured liquid contact angles by the software **Matlab R2011b** (MathWorks, America). The sum of γ_S^d , γ_S^p was considered as the membrane surface free energy.

The pore size and pore size distribution of the prepared membranes were investigated using a Capillary Flow Porometer Porolux 1000 (Porolux, Belgium) by the gas–liquid displacement method [39]. The overall porosity was determined by gravimetric method. The membrane coupon was immersed to ethanol solution

Table 2

Surface free energy and polarity nature of the reagents for CA measurement.

Reagent	γ_L^p	γ_L^d	γ_L	γ_L^p/γ_L^d	Polarity
Water	51	21.8	72.8	2.36	Polar
Glycerol	26.4	37	63.4	0.71	Polar
Diiodomethane	2.3	48.5	50.8	0.05	Non-polar

Note: γ_L is the surface free energy of the liquid, γ_L^d and γ_L^p represent the dispersion force term and polar force term of the liquid, respectively.

and ultrapure water in sequence (24 h for each liquid). The porosity ε was calculated as follows:

$$\varepsilon = \frac{(M_w - M_d)/\rho_w}{(M_w - M_d)/\rho_w + M_d/\rho_p} \quad (2)$$

Where, M_w is the weight of the wet membrane, M_d is the weight of the dry membrane. ρ_w and ρ_p are the density of water and polymer powder, respectively.

2.6. Direct contact membrane distillation (DCMD) test

The as-prepared hydrophobic membranes were applied for DCMD desalination to evaluate their performance, and the setup of the DCMD could be found in Fig. 1, which was same as the previous work [27] by adding a computer automatic recording unit. A super thermostat bath and a cryostat were used for temperature controlling. The membrane with an effective area of 5.218×10^{-3} m² was tightly clamped in the flat-sheet membrane module. The feed solution (35 g/L NaCl solution) was in contact with the upper layer of membranes (PVDF-CTFE top layer) and distilled water (about 30 μS/cm) was in contact with PET supporting layer acting as the condensate water, both sides were circulated by two magnetic pumps. The flow rate of the feed and permeate were kept constant at 65 L/h and 50 L/h. The temperature of the permeate inlet was kept at 20 °C and the feed temperature was changed from 40 °C to 80 °C. The concentration of NaCl in permeate was obtained by conductivity measurement, and the conductivity and permeate weight was record at set intervals.

The permeate flux J was calculated by the following equation.

$$J = \frac{m}{A \cdot t} \quad (3)$$

Where, J represents the permeate flux (kg/m² h), m is the permeate weight (kg), A is the effective area of membrane (m²) and t represents the sampling time (h).

A 120 h continuous DCMD test was also performed to assess the sustainability of the prepared membrane. The same DCMD setup was applied under same operation condition, while the temperature of the feed side was kept at 50 °C. The conductivity and permeate weight was record at set intervals.

3. Results and discussions

3.1. Cloud point of the casting solution

The cloud point of each casting solution was shown in Fig. 2, together with the titrimetric content of non-solvent (H₂O). It clearly showed that the solution M1 prepared by single PEG exhibited the highest stability. When LiCl was added to PEG-containing solution, the cloud point significantly transferred closer to solvent-additives axis and the non-solvent content decreased from 5.14 g to 3.3 g, indicating that the solution stability decreased as LiCl dosage increased. The water tolerance of solution M9 was

Fig. 1. Schematic diagram of the DCMD setup: 1. Super thermostat bath 2. Feed solution 3. Magnetic pump 4. Valve 5. Rotameter 6. Flat-sheet membrane module 7. Cryostat 8. Permeate collector 9. Conical flask 10. Balance 11. Computer recording system 12. Display t. Thermometer c. Conductivity meter.

Fig. 2. Cloud point of the casting solutions.

significantly lower than that of M1, and the addition of PEG possessed slightly influence as it was parallel to the solvent–additives axis if a line was plotted by the cloud point of solution M6 to M9. It illustrated that although both PEG and LiCl reduced the thermodynamic miscibility of the casting solution, the effect of LiCl was more significant. The reason may be the formation of acid–base complexes between the LiCl and DMAc and the interaction between Li⁺ ions and electron donor groups of VDF [36,40,41].

It is well acknowledged that the phase inversion process was more complex for semi-crystalline polymer [42,43], the S–L demixing and L–L demixing compete during phase inversion. In the titration experiment, it was found that all the solutions turned to gel state at the titration end point, which pointed out that the gelation and crystallization induced S–L demixing occurred. It means that the PVDF-CTFE had strong potentiality to crystallization during membrane formation process, however the

crystallization degree varied for different solution by different mixed additives. As both L–L and S–L demixing play an important role on membrane morphology and pore structure, it was safe to infer that the resultant membranes properties and performance would differ greatly.

3.2. Membrane morphology

3.2.1. Effects of LiCl

The effects of LiCl on the PVDF-CTFE (12 wt%)/PEG (5 wt%)/DMAc ternary system were investigated, and the morphology of membrane surface and cross-section were presented in Fig. 3. All membranes presented typical asymmetric structure composed by top layer, macrovoids and sponge-like sub-layer which was generally formed by the L–L demixing during instantaneous phase inversion. However, crystallites appeared in both membrane

Fig. 3. The effects of LiCl on the PVDF-CTFE/PEG/DMAc ternary solution: (A) membrane surface; (B) the entire cross-section; (C) macrovoids near top surface.

surface and cross-section with the addition of LiCl. The pore interconnectivity of top-layer (I), macrovoids layer (II), and sponge-like layer (III) increased as the LiCl dosage increased, which clearly illustrated in Fig. 3C. The pore structure turned from non-porous walls (M1) into particulate packed structure as LiCl was added, especially for M4. This result demonstrated that the S–L demixing

possessed more significant influences as LiCl dosage increased. For membrane surface, it can be also found that the pore interconnectivity increased along with the LiCl dosage. So it was safe to infer that PEG benefited the I–L demixing process result from its strong pore-forming effect and instantaneous phase inversion process, while LiCl facilitated the S–L demixing process especially

Fig. 4. The effects of PEG on the PVDF-CTFE/LiCl/DMAc ternary solution: (A) membrane surface; (B) the entire cross-section; (C) macrovoids near top surface.

the crystallization due to the strong interaction between LiCl and other components.

From the kinetic point of view, the addition of additives can also reduce the phase inversion rate by increasing the viscosity of solution. Moreover, the viscosity growth by LiCl addition will induce pre-gelation process before coagulation due to the strong interaction among LiCl, DMAc, and PVDF-CTFE [44,45]. The pre-gelation would result in S–L demixing of the casting solution, which benefited the polymer crystallization process in coagulation bath. Hence it was also believed to be another reason for the higher interconnectivity pore structure and the occurrence crystallites as shown in Fig. 3.

3.2.2. Effects of PEG

The effects of PEG on PVDF-CTFE (12 wt%)/LiCl (5 wt%)/DMAc ternary system were also investigated, the membrane morphology were shown in Fig. 4. It is interesting to found that the membrane

prepared by single LiCl presented remarkable different structure compared to the membrane prepared by single PEG. The membrane displayed almost symmetric cross-section with better pore interconnectivity, while M1 showed asymmetric structure with non-porous pore wall in the whole cross-section. The pre-gelation process and the effect on phase inversion process induced by LiCl were attributed to this structure as the solidification process appeared before coagulation. Meanwhile, the macrovoids were suppressed due to the slowly phase inversion process, as a result the symmetric structure was formed.

It was also worth mentioning that the influence was more slightly when PEG was added to LiCl-containing solution. Furthermore, the membrane morphology showed no obvious variation as PEG dosage increased. However, the macrovoids in cross-section increased as 1 wt% PEG was added due to the pore-forming effect of PEG. As more PEG was added, the macrovoids were then suppressed. Furthermore, the structure in macrovoids (II) was

similar to the sponge-like layer (III) as shown in M6–M9. However, it displayed different structure in layer (II) and layer (III) for membranes M1–M4 prepared with 5 wt% PEG, although the addition of LiCl mitigate this difference. The high viscosity of casting solution was responsible for the suppression due to the higher content of additives and lower content of solvent, especially when dosage of strong additives LiCl was 5 wt%. Thus the exchange rate of solvent and non-solvent would decrease during coagulation process, as a result the interconnected structure was formed even in macrovoids. Meanwhile, the pre-gelation would possess more influence for casting solution with high viscosity, which acted as another reason for the particle packed structure of membranes prepared by LiCl, especially when PEG was added.

3.2.3. Membrane morphology of M5

The membrane prepared by solution M5 was labeled as membrane M5, which containing 4 wt% of PEG and LiCl. The surface morphology of M5 was shown in Fig. 3. The pores in membrane surface were more uniform without significant big pores as compared to membranes M2–M4. Thus high rejection and anti-wetting property might be expected. For membrane cross-section, macrovoids were suppressed due to the slow phase inversion process as discussed before. Meanwhile, the particulate packed pore structure with high interconnectivity was shown. Similar morphology was reported in our previous work, in which a comparison between hydrophobic membranes by PVDF and PVDF-CTFE was conducted with/without additives [27]. In that work, it also demonstrated that the S–L demixing process showed more influence when additives was added as compared to the membrane without additives. So the pore interconnectivity in both membrane surface and cross-section was higher. Thus, it was sure that the additives addition would highly influence the phase inversion process and the membrane was more suitable for MD application than the membrane prepared without additives according to that finding.

It was also interesting to find that the structure of M5 in macrovoids (II) was similar to the sponge-like layer (III), same to membranes M6–M9. It indicated that the S–L demixing dominated the phase inversion process during membrane formation. Based

on this structure, high flux can also be expected because the interconnected pore structure could offer more passages for vapor transfer. Furthermore, the sustainability can be high due to lacking of big macrovoids. In a word, it was believed that high permeability and sustainability could be offered by M5 due to its morphology and pore structure.

3.3. Membrane surface analysis

Fig. 5 showed the FT-IR spectrograms of the resultant membranes and the PVDF-CTFE copolymer. The similar waveforms indicated that the molecular structure of PVDF-CTFE did not change during the membrane formation process. More importantly, it can be infer that the solvent and additives were completely removed from membrane.

AFM was employed to study the membranes surface structure and the results were presented in Fig. 6. The crystallites were clearly evidenced in the surface of each membrane. While the membrane prepared with single PEG additive showed the smoothest surface, suggesting the lowest crystallization propensity. And the polymer crystallization became more significant when LiCl was added, which was in accordance with the SEM images. The membrane prepared by single LiCl additive showed more crystalline structure as compared to membrane by single PEG additive, indicating a stronger interaction between LiCl and the solvent or the polymer. The crystallization propensity also became higher when PEG was added, the increased viscosity was believed to be the reason as discussed in Section 3.2.

It was also found that the network pores dominated in membrane surface especially in M1, indicating that the L–L demixing process dominated the phase inversion process as confirmed by SEM observation. However, every membrane showed sign of polymer crystallization especially when LiCl dosage increased. That further affirmed the S–L demixing showed more important influence as the LiCl dosage increased.

The roughness of membrane was also obtained by AFM and it was presented in Table 3. The smoothest surface was observed on the membrane prepared with single PEG additive, and the membrane roughness increased as LiCl dosage increased. The

Fig. 5. FT-IR spectrograms of the PVDF-CTFE powder and membranes.

Fig. 6. 3-D morphology and depth distribution of the PVDF-CTFE membranes surface.

Table 3
Surface roughness of the PVDF-CTFE flat-sheet membranes by LiCl/PEG mixed additives.

Membrane code	R_a (nm)	R_q (nm)	R_{max} (nm)
M1	24.473	30.650	216.002
M3	31.099	40.743	291.893
M5	34.113	43.362	314.247
M7	40.602	52.616	354.098
M9	37.435	47.515	315.749

crystallites and pore structure in membrane surface may be the reason for the improvement of membrane roughness. Correspondingly, the membrane prepared by single LiCl additive possess higher roughness than the counterpart with single PEG additive. And the roughness also increased when PEG was added due to the higher viscosity when additives with higher content was added.

It has been confirmed that the membrane pore structure, roughness and the crystallites in membrane surface have tremendous impacts on membrane hydrophobicity [31,46,47]. In this study, the contact angles with water, glycerol, and diiodomethane were measured to indicate the membrane hydrophobicity, and the results were presented in Table 4. Clear evidence was found that increasing the LiCl content in the PEG-containing casting solutions increased the membrane hydrophobicity, while increasing the PEG content in the LiCl-containing casting solution reduced the membrane hydrophobicity. And a clear correlation was found between the membrane surface roughness and membrane hydrophobicity, which further verified the causation between membrane roughness and hydrophobicity. However, although the hydrophobicity may be increased for the crystals in membrane surface, the addition of PEG may decreased the hydrophobicity as an opposite factor. That can be the reason why M7 showed slightly lower contact angle than M5 and M9 although the roughness was higher. Based on the contact angles, the surface free energy of resultant membranes was also calculated and presented in Table 4. It is obvious that the surface free energy was consistent with membrane hydrophobicity with an exactly opposite trend.

3.4. Porosity, pore size and pore distribution

As pore structure is a crucial factor for membrane permeability, the overall porosity, pore size and pore size distribution were applied together to characterizing the pore structure of the resultant membranes. The overall porosity, bubble point pore size, smallest pore size, and mean pore size of the flat-sheet membranes can be found in Table 5. It is clear that the porosity increased along with the increasing LiCl content, which can be rationalized by the interconnected particle packed structure caused by the polymer crystallization as shown in Fig. 3. However, when a small amount of PEG was added to solution, the porosity also

increased. Such an effect can be attributed to the strong pore forming effect and the crystallization effect of the mixed additives PEG/LiCl. But the pore size and porosity decreased when more PEG was added, which can be ascribed to the higher viscosity. The results also further verified that LiCl could suppress the growth of macrovoids, which resulted in the decrease of bubble point pore size. In addition, the membrane M5 showed the smallest pore size, which still possessed considerable porosity. This structure was believed to be suitable for MD process as high flux as well as high rejection can be offered.

Fig. 7 presents the pore size distribution of the flat sheet membranes, where the percent flow representing the number of relevant pores was plotted against the pore size (μm). All the flat sheet membranes showed narrow pore size distribution. Increasing the LiCl dosage led to a broader distribution (as M1–M4 shown), which may be caused by the partial phase inversion and pre-gelation as the content of additives was high. A same trend can be found as PEG was added to LiCl-containing solution. However, M5 showed narrow pore distribution although the content of additives was same as M4 and M6. The synergistic effect of PEG and LiCl was considered as the reason.

3.5. Membrane distillation performance

The MD desalination performance of prepared membranes was also listed in Table 5. Lowest flux was observed for the membrane M1, and the permeate flux increased along with the increasing dosage of LiCl. Membrane M9 offered a higher flux as compared to membrane M1, and the permeability also further improved when PEG was added. At the same time, the membranes prepared by 5 wt% LiCl (M6–M9) present higher permeate flux as compared to the counterpart prepared by 5 wt% PEG (M1–M4). The higher flux was attributed to the interconnected pore structure which could provide abundant passage for the transmission of permeate vapors and possess better permeability when mixed additives was used.

M5 offered a flux of $23.57 \text{ kg/m}^2 \text{ h}$ with a low permeate conductivity of $5 \mu\text{S/cm}$, which was believed to have the optimal properties and performance. That was confirmed by the pore structure and hydrophobicity as discussed before. So it was selected to study the membrane anti-wetting property and sustainability by a 120 h continuous DCMD test with the same DCMD setup. Fig. 8 showed the result of the continuous MD test, the flux decreased from 23.57 to $21.33 \text{ kg/m}^2 \text{ h}$, i.e., less than 10% decline during the operation. Meanwhile, the conductivity still kept lower than $11 \mu\text{S/cm}$, indicating a rejection higher than 99%. Specifically, the flux kept steady and the conductivity decreasing quickly from $28 \mu\text{S/cm}$ (the conductivity of the initial distilled water) to $5 \mu\text{S/cm}$ during the first 24 h, indicating a high permeate flux with low conductivity. The $5 \mu\text{S/cm}$ can be considered as the conductivity of the permeate stream in assuming that the initial distilled water was completely discharged after 24 h, as the total permeate volume was about 3.0 m^3 which was about 5 times larger than

Table 4
CA with different reagents and the surface free energy of flat-sheet membranes by LiCl/PEG mixed additives.

Membrane code	CA_{water} (deg)	$\text{CA}_{\text{glycerol}}$ (deg)	$\text{CA}_{\text{diiodomethane}}$ (deg)	$\gamma (\times 10^{-5} \text{ N cm}^{-1})$
M1	91.53 ± 3.5	79.92 ± 2.3	57.13 ± 1.4	34.57
M2	92.23 ± 2.2	81.83 ± 1.7	57.73 ± 1.3	33.62
M3	92.58 ± 4.9	82.04 ± 3.3	58.03 ± 1.5	33.36
M4	95.40 ± 5.3	84.93 ± 3.3	59.10 ± 2.5	31.44
M5	98.70 ± 1.8	88.50 ± 2.0	60.80 ± 0.9	29.30
M6	95.24 ± 2.7	84.68 ± 1.4	58.68 ± 1.7	31.68
M7	96.45 ± 3.4	86.93 ± 1.8	59.03 ± 0.9	30.74
M8	98.82 ± 2.8	87.74 ± 1.6	60.75 ± 1.3	29.32
M9	101.83 ± 4.4	90.83 ± 2.6	63.44 ± 2.6	27.26

Table 5

Pore size, porosity, and MD performance of the PVDF-CTFE flat-sheet membranes by LiCl/PEG mixed additives.

Code	Bubble point pore size (μm)	Smallest pore size (μm)	Mean pore size (μm)	Porosity (%)	MD flux ^{a1} ($\text{kg}/\text{m}^2 \text{ h}$)	Conductivity ($\mu\text{S}/\text{cm}$)
M1	0.37	0.110	0.114	61.18 ± 2.5	17.59 ± 0.6	25
M2	0.21	0.084	0.126	64.71 ± 1.7	21.33 ± 0.5	11
M3	0.27	0.087	0.135	67.20 ± 3.1	22.59 ± 0.1	18
M4	0.35	0.104	0.137	72.81 ± 1.7	22.84 ± 0.2	9
M5	0.33	0.096	0.102	70.64 ± 1.0	23.57 ± 0.2	5
M6	0.26	0.082	0.107	71.15 ± 1.3	22.32 ± 0.8	18
M7	0.29	0.092	0.129	72.15 ± 3.3	23.57 ± 0.3	12
M8	0.33	0.098	0.135	72.24 ± 1.8	22.84 ± 0.5	9
M9	0.20	0.090	0.130	70.79 ± 0.9	22.08 ± 0.9	7

^a The operation temperature of the feed and permeate were kept at 50 °C and 20 °C, respectively. **Fig. 7.** Pore size distribution of the PVDF-CTFE membranes prepared by PEG/LiCl mixed additives.

volume of the permeate collector (about 0.48 m^3).

3.6. Comparison with other flat-sheet MD membranes

The effect of operation temperature on MD performance was also studied and shown in Fig. 9. The MD flux was significantly increased from 12.20 to $62.09 \text{ kg}/(\text{m}^2 \text{ h})$ as temperature increased from 40 to 80 °C. However, the salt rejection was higher than 99.9% under each operation temperature.

Based on the performance under different temperature, a comparison with the flat-sheet membranes reported in the recent four years was carried out and listed in Table 6 [31,48–61]. It can be found that the PVDF-CTFE membrane prepared in this work presented higher permeate flux in MD desalination application except PES and PSf membranes modified by CF4 plasma. As which also showed excellent salt rejection even during the 120 h continuous operation, it was safe to say that PVDF-CTFE copolymer has noteworthy potential for hydrophobic membrane preparation and application, especially when mixed additives were used.

3.7. The effects of other mixed additives

Other additives including PVP, H_3PO_4 , glycerol, and H_2O were also mixed with LiCl and used as additives for PVDF-CTFE membrane in this work. The membranes morphology observed by FESEM were shown in Fig. 10. The membrane M10 prepared by PVP/LiCl mixed additive showed poorly distributed pores on the membrane surface, large macrovoids throughout the cross-section were also appeared on this membrane. The instantaneous phase inversion and the dominating L–L demixing were believed to be the reasons for such structures. However, loose packed pore structure were also found in the wall of the macrovoids, which may be induced by the interaction of LiCl and PVP. H_3PO_4 and glycerol also showed pore-forming effects during membrane preparation when they were mixed with LiCl, showed typical asymmetric structure induced by L–L demixing. However, the crystallites can also be found in sponge-like layer, which indicates the effect of S–L demixing. However, the membrane M10 possessed higher interconnectivity in both membrane surface and cross-section. H_3PO_4 has been proved to benefit the PVDF crystallization process due to the strong interaction between H_3PO_4 and other component [62], which can explain the higher interconnectivity

Fig. 8. Permeate flux and conductivity of PVDF-CTFE membrane during a 120-h continuous MD operation (feed temperature: 50 °C, permeate temperature: 20 °C).

when H_3PO_4 was used as additive for PVDF-CTFE membrane. As a strong non-solvent, when H_2O was used as a co-additive with LiCl, the resultant membrane showed more symmetric cross-section. And the crystallites apparently showed in both membrane surface and cross-section, indicating the S–L demixing dominated the phase inversion process. Pre-gelation process has a strong trend to occur when H_2O was added because H_2O may even act as the nucleus for solidification process. In a word, the interconnectivity by different additives should be $\text{H}_2\text{O} > \text{H}_3\text{PO}_4 > \text{PVP} > \text{glycerol}$ as shown in Fig. 10, which was result from the phase inversion process.

Other properties of these membranes were presented in Table 7. It was clear that the addition of all these four co-additives resulted in the decrease in membrane hydrophobicity, especially for PVP and glycerol. The membrane with PVP showed the largest pore size and porosity. While the membrane with glycerol also had large pores and broad pore size distribution, but the porosity was low. That can be explained by the low interconnectivity structure. However, membranes prepared by $\text{H}_3\text{PO}_4/\text{LiCl}$ and $\text{H}_2\text{O}/\text{LiCl}$ mixed additives showed uniform pore distribution.

Fig. 11 shows the DCMD performance of membranes prepared by mixed additives. M10 had the highest flux while M12 offered the lowest flux, which was consistent with their porosity. It also worth mentioning that the permeate conductivity was high and kept increase gradually as the MD process proceeding for M10, indicating that it is not suitable for MD application. M11 and M13 had similar flux due to the similar pore structure, which was around $22.5 \text{ kg}/(\text{m}^2 \text{ h})$ when feed temperature was 50 °C. However, it is sure that the flux was higher than membrane prepared by single LiCl. That means the application of mixed additives can somehow increase MD performance because of the synergistic effect of different additives.

4. Conclusions

In the present work, PVDF-CTFE copolymer was applied to hydrophobic membrane preparation for MD application. PEG/LiCl mixed additives were comprehensively studied in terms of different mixing ratios. The results revealed that the L–L demixing dominated

Fig. 9. The effect of temperature on MD performance of PVDF-CTFE membrane (permeate temperature was kept at 20 °C).

Table 6

Comparison of permeate flux in this study with other reported flat-sheet membrane in DCMD process in the recent four years.

Membrane	Feed solution		Permeate solution			Permeate flux (kg/m ² h)	Salt rejection /permeate cond. ^c	Refs.
	Types ^a	Temp. ^b (°C)	Flow rate (L/h)/ Velocity (m/s)	Temp. (°C)	Flow rate (L/h)/velocity (m/s)			
PVDF(VIPS)	35 g/L	73	54 L/h	25	54 L/h	18.9	> 99.7%	48
PES (CF4 plasma modified)	4 wt%	63.3	0.36 m/s	20	0.36 m/s	45.4	99.80%	49
PVDF	3.5 wt%	80.5	70 L/h	20	70 L/h	47.6	> 99.9%	50
PVDF-HFP (electrospun)	10 g/L	65	900 L/h	24	900 L/h	22	98%	51
PSf (VIPS)	35 g/L	73	108 L/h	25	27 L/h	30	< 40 μS/cm	52
¹ PVDF-PDMS-SiO ₂ ² PVDF	3.5 wt%	70	–	20	–	14 8.25	2 μS/cm	53
PVDF	35 g/L	50	70 L/h	20	70 L/h	12.5	2 μS/cm	31
PTFE (GE) PVDF-HFP/PAN (dual-layer electrospun)	35 g/L	60	24 L/h	20	24 L/h	20	7.5 μS/cm	54
¹ PVDF(CF4 plasma modified)	4 wt%	57.8	0.17 m/s	21.3	0.17 m/s	30	99.90%	55
² PVDF(Ar modified)						23.47	> 98.5%	
PVDF(millipore)	seawater(conc. B= 5.37 mg/L)	74	20	20	20	16.68	99.97%	56
PTFE (Sterlitech)	35 g/L	70	90 L/h	30	90 L/h	27.5	Boron: 0.47 mg/L	
PVDF	Seawater (65 mS/cm)	65	16 L/h	25	16 L/h	18	99.9%	57
							> 99%	58
MWCNT/PVDF	35 g/L	82	2.88 L/h	20	2.88 L/h	34.2	100%	59
PSf (CF4 plasma modified)	4 wt%	60.2	36 L/h	20	36 L/h	32.58	99.99%	60
PVDF(CO ₂ induced inversion)	0.1 M	–	–	–	–	10.191	96.71%	61
PVDF-CTFE	35 g/L	50	65 L/h	20	50 L/h	23.57	5μS/cm	This work

^a The feed solution is NaCl solution which only the concentration is list if there is no detailed description.^b “Temp.” represents the “temperature”.^c “cond.” represents the “conductivity”.

the coagulation process, but each of them showed sign of crystallization as PVDF-CTFE was easily crystallized in these system. However, the degree of crystallization was variable. PEG is an effective pore-form agent and benefits the L–L demixing, while LiCl is beneficial for S–L demixing especially when being combined with other additives. The addition of LiCl in PEG-containing solution significantly benefited the polymer crystallization process, and the hydrophobicity, porosity, pore interconnectivity, and MD performance were significantly increased. While the addition of PEG in LiCl-containing solution has slightly influences. PEG/LiCl with a mix ratio at 4:4 was identified to be the best mixed additives for PVDF-CTFE membrane preparation. The water contact angle, surface free energy, overall porosity, mean pore size, MD flux, and permeate conductivity of this membrane were 98.7°, $29.3 \times 10^{-5} \text{ N cm}^{-1}$, 70.64%, 0.1022 μm, 62.09 kg/(m² h), and 5 μS/cm, respectively. And the membrane kept steady MD performance in the 120 h continuous test without severe membrane wetting.

Other types of additives including PVP, H₃PO₄, glycerol, and H₂O were also mixed with LiCl to study the effect of mixed additives. It was found that PVP and glycerol might significantly promote the pore size and reduce the hydrophobicity, which were even not suitable for MD process. However, the addition of H₃PO₄ and H₂O could improve the MD performance because of the polymer crystallization.

The results presented in this work clearly demonstrated that by carefully tuning the additive ratio, hydrophobic PVDF-CTFE has a bright prospect in hydrophobic membrane preparation, which can be prepared with optimal structure suitable for MD process. And the application of mixed additives can be a very effective way to modify hydrophobic membrane property and performance. However, more works need to be carried out to obtain ideal PVDF-CTFE hydrophobic membrane, including finding appropriate casting solution system for PVDF-CTFE, preparing PVDF-CTFE membrane in other type and exploring proper mixed additives.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant nos. 51378491, 51578533, and 21307149).

Nomenclature

γ_s	the surface energy of the solid
γ_L	the surface energy of the liquid
γ_s^d	the dispersion force of the solid
γ_s^p	the polar force of the solid
γ_L^d	the dispersion force of the liquid
γ_L^p	the polar force of the liquid
θ	contact angle
ε	the membrane porosity
M_w	the weight of the wet membrane
M_d	the weight of the dry membrane
ρ_w	the density of water
ρ_p	the density of membrane
J	the permeate flux
M	the quantity of permeate
A	membrane effective area
t	the sampling time
R	the rejection coefficient
C_f	the salt concentrations of the feed
C_p	the salt concentrations of the permeate
R_a	the average roughness
R_q	the root mean square roughness
R_{max}	the maximum roughness

Fig. 10. Surface and cross-section morphology of the PVDF-CTFE membranes prepared by other LiCl-based additives.

Table 7
Properties of the membranes prepared by other LiCl-based mixed additives.

Membrane code	CA _{water} (deg)	Bubble point pore size (μm)	Smallest pore size (μm)	Mean pore size (μm)	Porosity (%)
M9	101.83 ± 4.4	0.20	0.090	0.130	70.79 ± 0.9
M10	85.42 ± 2.6	4.61	0.393	0.456	82.71 ± 3.6
M11	90.85 ± 2.3	0.27	0.140	0.171	70.91 ± 1.4
M12	80.73 ± 1.7	0.64	0.209	0.228	67.33 ± 1.5
M13	87.67 ± 1.5	0.25	0.141	0.158	71.14 ± 2.4

Fig. 11. DCMD performance of the PVDF-CTFE membranes prepared by other LiCl-based additives (Feed temperature: 50 °C, permeate temperature: 20 °C).

References

- [1] K.W. Lawson, D.R. Lloyd, Membrane distillation, *J. Membr. Sci.* 124 (1997) 1–25.
- [2] E. Curcio, E. Drioli, Membrane distillation and related operations—a review, *Sep. Purif. Rev.* 34 (2005) 35–86.
- [3] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, *Desalination* 356 (2015) 56–84.
- [4] F. Spyropoulos, D.M. Lloyd, R.D. Hancock, A.K. Pawlik, Advances in membrane emulsification. Part A: recent developments in processing aspects and microstructural design approaches, *J. Sci. Food Agric.* 94 (2014) 613–627.
- [5] C. Charcosset, I. Limayem, H. Fessi, The membrane emulsification process—a review, *J. chem. technol. biotechnol.* 79 (2004) 209–218.
- [6] N.M. Kocherginsky, Q. Yang, L. Seelam, Recent advances in supported liquid membrane technology, *Sep. Purif. Technol.* 53 (2007) 171–177.
- [7] C. Zambra, J. Romero, L. Pino, A. Saavedra, J. Sanchez, Concentration of cranberry juice by osmotic distillation process, *J. Food Eng.* 144 (2015) 58–65.
- [8] E. Drioli, G. Di Profio, E. Curcio, Progress in membrane crystallization, *Curr. Opin. Chem. Eng.* 1 (2012) 178–182.
- [9] S. Mosaddegh-Sedghi, D. Rodrigue, J. Brisson, M.C. Iliuta, Wetted phenomenon in membrane contactors—causes and prevention, *J. Membr. Sci.* 452 (2014) 332–353.
- [10] X. Li, C. Wang, Y. Yang, X. Wang, M. Zhu, B.S. Hsiao, Dual-biomimetic superhydrophobic electrospun polystyrene nanofibrous membranes for membrane distillation, *ACS Appl. Mater. Interfaces* 6 (2014) 2423–2430.
- [11] S. Nejadi, C. Boo, C.O. Osuji, M. Elimelech, Engineering flat sheet microporous PVDF films for membrane distillation, *J. Membr. Sci.* 492 (2015) 355–363.
- [12] Z. Cui, E. Drioli, Y.M. Lee, Recent progress in fluoropolymers for membranes, *Prog. Polym. Sci.* 39 (2014) 164–198.
- [13] B. Ameduri, From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: recent developments and future trends, *Chem. Rev.* 109 (2009) 6632–6686.
- [14] C. Feng, B. Shi, G. Li, Y. Wu, Preparation and properties of microporous membrane from poly (vinylidene fluoride-co-tetrafluoroethylene) (F2. 4) for membrane distillation, *J. Membr. Sci.* 237 (2004) 15–24.
- [15] L. Guo, Y. Liu, C. Zhang, J. Chen, Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr (VI) transport, *J. Membr. Sci.* 372 (2011) 314–321.
- [16] C.M. Costa, A. California, V. Cardoso, V. Sencadas, L. Rodrigues, M. Silva, S. Lanceros-Méndez, Electroactive poly (vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) microporous membranes for lithium-ion battery applications, *Ferroelectrics* 430 (2012) 103–107.
- [17] C. Feng, R. Wang, B. Shi, G. Li, Y. Wu, Factors affecting pore structure and performance of poly (vinylidene fluoride-co-hexafluoro propylene) asymmetric porous membrane, *J. Membr. Sci.* 277 (2006) 55–64.
- [18] L. Shi, R. Wang, Y. Cao, C. Feng, D.T. Liang, J.H. Tay, Fabrication of poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) asymmetric microporous hollow fiber membranes, *J. Membr. Sci.* 305 (2007) 215–225.
- [19] L. Shi, R. Wang, Y. Cao, D.T. Liang, J.H. Tay, Effect of additives on the fabrication of poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) asymmetric microporous hollow fiber membranes, *J. Membr. Sci.* 315 (2008) 195–204.
- [20] F. Boschet, B. Ameduri, (Co)polymers of chlorotrifluoroethylene: Synthesis, properties, and applications, *Chem. Rev.* 114 (2013) 927–980.
- [21] Y.W. Kim, J.K. Choi, J.T. Park, J.H. Kim, Proton conducting poly (vinylidene fluoride-co-chlorotrifluoroethylene) graft copolymer electrolyte membranes, *J. Membr. Sci.* 313 (2008) 315–322.
- [22] J.H. Koh, Y.W. Kim, J.T. Park, B.R. Min, J.H. Kim, Nanofiltration membranes based on poly (vinylidene fluoride-co-chlorotrifluoroethylene)-graft-poly (styrene sulfonic acid), *Polym. Adv. Technol.* 19 (2008) 1643–1648.
- [23] Y.W. Kim, J.T. Park, J.H. Koh, D.K. Roh, J.H. Kim, Anhydrous proton conducting membranes based on crosslinked graft copolymer electrolytes, *J. Membr. Sci.* 325 (2008) 319–325.
- [24] J.H. Koh, Y.W. Kim, J.T. Park, J.H. Kim, Templated synthesis of silver nanoparticles in amphiphilic poly (vinylidene fluoride-co-chlorotrifluoroethylene) comb copolymer, *J. Polym. Sci. Part B: Polym. Phys.* 46 (2008) 702–709.
- [25] J.H. Koh, J.A. Seo, J.T. Park, J.H. Kim, Synthesis and characterization of AgBr nanocomposites by templated amphiphilic comb polymer, *J. Colloid Interface Sci.* 338 (2009) 486–490.
- [26] F. Liu, M.R.M. Abed, K. Li, Hydrophilic modification of P (VDF-co-CTFE) porous membranes, *Chem. Eng. Sci.* 66 (2011) 27–35.
- [27] J. Wang, L. Zheng, Z. Wu, Y. Zhang, X. Zhang, Fabrication of hydrophobic flat sheet and hollow fiber membranes from PVDF and PVDF-CTFE for membrane distillation, *J. Membr. Sci.* 497 (2016) 183–193.
- [28] A.L. Ahmad, A.A. Abdulkarim, B.S. Ooi, S. Ismail, Recent development in additives modifications of polyethersulfone membrane for flux enhancement, *Chem. Eng. J.* 223 (2013) 246–267.
- [29] R. Naim, A.F. Ismail, A. Mansourizadeh, Effect of non-solvent additives on the structure and performance of PVDF hollow fiber membrane contactor for CO₂ stripping, *J. Membr. Sci.* 423–424 (2012) 503–513.
- [30] A. Mansourizadeh, A.R. Pouranfar, Microporous polyvinylidene fluoride hollow fiber membrane contactors for CO₂ stripping: Effect of PEG-400 in spinning dope, *Chem. Eng. Res. Des.* 92 (2014) 181–190.
- [31] D. Hou, H. Fan, Q. Jiang, J. Wang, X. Zhang, Preparation and characterization of PVDF flat-sheet membranes for direct contact membrane distillation, *Sep. Purif. Technol.* 135 (2014) 211–222.
- [32] S. Wongchitphimon, R. Wang, R. Jiratananon, L. Shi, C.H. Loh, Effect of polyethylene glycol (PEG) as an additive on the fabrication of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) asymmetric microporous hollow fiber membranes, *J. Membr. Sci.* 369 (2011) 329–338.
- [33] E. Fontananova, J.C. Jansen, A. Cristiano, E. Curcio, E. Drioli, Effect of additives in the casting solution on the formation of PVDF membranes, *Desalination* 192 (2006) 190–197.
- [34] E. Yuliwati, A.F. Ismail, Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment, *Desalination* 273 (2011) 226–234.
- [35] D. Hou, J. Wang, X. Sun, Z. Ji, Z. Luan, Preparation and properties of PVDF composite hollow fiber membranes for desalination through direct contact membrane distillation, *J. Membr. Sci.* 405–406 (2012) 185–200.
- [36] D. Hou, J. Wang, D. Qu, Z. Luan, X. Ren, Fabrication and characterization of hydrophobic PVDF hollow fiber membranes for desalination through direct contact membrane distillation, *Sep. Purif. Technol.* 69 (2009) 78–86.
- [37] A.C. Sun, W. Kosar, Y. Zhang, X. Feng, A study of thermodynamics and kinetics pertinent to formation of PVDF membranes by phase inversion, *Desalination* 309 (2013) 156–164.
- [38] D.K. Owens, R. Wendt, Estimation of the surface free energy of polymers, *J. Appl. Polym. Sci.* 13 (1969) 1741–1747.
- [39] L. García-Fernández, M.C. García-Payo, M. Khayet, Effects of mixed solvents on the structural morphology and membrane distillation performance of PVDF-HFP hollow fiber membranes, *J. Membr. Sci.* 468 (2014) 324–338.
- [40] J. Kong, K. Li, Preparation of PVDF hollow-fiber membranes via immersion precipitation, *J. Appl. Polym. Sci.* 81 (2001) 1643–1653.
- [41] C.H. Loh, R. Wang, Insight into the role of amphiphilic pluronic block copolymer as pore-forming additive in PVDF membrane formation, *J. Membr. Sci.* 446 (2013) 492–503.
- [42] M. Mulder, Basic principles of membrane technology, Springer Science & Business Media, 1996.
- [43] D.J. Lin, K. Beltsios, T.H. Young, Y.S. Jeng, L.P. Cheng, Strong effect of precursor preparation on the morphology of semicrystalline phase inversion poly(vinylidene fluoride) membranes, *J. Membr. Sci.* 274 (2006) 64–72.
- [44] D. Wang, K. Li, W.K. Teo, Porous PVDF asymmetric hollow fiber membranes prepared with the use of small molecular additives, *J. Membr. Sci.* 178 (2000) 13–23.
- [45] K.Y. Lin, D.M. Wang, J.Y. Lai, Nonsolvent-induced gelation and its effect on membrane morphology, *Macromolecules* 35 (2002) 6697–6706.
- [46] M. Rafat, D. De, K. Khulbe, T. Nguyen, T. Matsura, Surface characterization of hollow fiber membranes used in artificial kidney, *J. Applied Polym. Sci.* 101 (2006) 4386–4400.
- [47] Q. Li, Z.L. Xu, M. Liu, Preparation and characterization of PVDF microporous membrane with highly hydrophobic surface, *Polym. Adv. Technol.* 22 (2011)

- 520–531.
- [48] H. Fan, Y. Peng, Application of PVDF membranes in desalination and comparison of the VMD and DCMD processes, *Chem. Eng. Sci.* 79 (2012) 94–102.
 - [49] X. Wei, B. Zhao, X.M. Li, Z. Wang, B.Q. He, T. He, B. Jiang, CF₄ plasma surface modification of asymmetric hydrophilic polyethersulfone membranes for direct contact membrane distillation, *J. Membr. Sci.* 407–408 (2012) 164–175.
 - [50] D. Hou, G. Dai, J. Wang, H. Fan, Z. Luan, C. Fu, Boron removal and desalination from seawater by PVDF flat-sheet membrane through direct contact membrane distillation, *Desalination* 326 (2013) 115–124.
 - [51] B.S. Lalia, E. Guillen-Burrieza, H.A. Arafat, R. Hashaiekeh, Fabrication and characterization of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) electrospun membranes for direct contact membrane distillation, *J. Membr. Sci.* 428 (2013) 104–115.
 - [52] Y. Peng, Y. Dong, H. Fan, P. Chen, Z. Li, Q. Jiang, Preparation of polysulfone membranes via vapor-induced phase separation and simulation of direct-contact membrane distillation by measuring hydrophobic layer thickness, *Desalination* 316 (2013) 53–66.
 - [53] J. Zhang, Z. Song, B. Li, Q. Wang, S. Wang, Fabrication and characterization of superhydrophobic poly (vinylidene fluoride) membrane for direct contact membrane distillation, *Desalination* 324 (2013) 1–9.
 - [54] L.D. Tijjng, Y.C. Woo, M.A.H. Johir, J.-S. Choi, H.K. Shon, A novel dual-layer bicomponent electrospun nanofibrous membrane for desalination by direct contact membrane distillation, *Chem. Eng. J.* 256 (2014) 155–159.
 - [55] C. Yang, X.M. Li, J. Gilron, D.F. Kong, Y. Yin, Y. Oren, C. Linder, T. He, CF₄ plasma-modified superhydrophobic PVDF membranes for direct contact membrane distillation, *J. Membr. Sci.* 456 (2014) 155–161.
 - [56] A. Boubakri, S.A.T. Bouguecha, I. Dhaouadi, A. Hafiane, Effect of operating parameters on boron removal from seawater using membrane distillation process, *Desalination* 373 (2015) 86–93.
 - [57] A. Kayvani Fard, Y.M. Manawi, T. Rhadfi, K.A. Mahmoud, M. Khraisheh, F. Benyahia, Synoptic analysis of direct contact membrane distillation performance in Qatar: a case study, *Desalination* 360 (2015) 97–107.
 - [58] J.A. Kharraz, M.R. Bilad, H.A. Arafat, Flux stabilization in membrane distillation desalination of seawater and brine using corrugated PVDF membranes, *J. Membr. Sci.* 495 (2015) 404–414.
 - [59] T.L.S. Silva, S. Morales-Torres, J.L. Figueiredo, A.M.T. Silva, Multi-walled carbon nanotube/PVDF blended membranes with sponge- and finger-like pores for direct contact membrane distillation, *Desalination* 357 (2015) 233–245.
 - [60] M. Tian, Y. Yin, C. Yang, B. Zhao, J. Song, J. Liu, X.-M. Li, T. He, CF₄ plasma modified highly interconnective porous polysulfone membranes for direct contact membrane distillation (DCMD), *Desalination* 369 (2015) 105–114.
 - [61] A. Zaherzadeh, J. Karimi-Sabet, S.M.A. Mousavian, S. Ghorbanian, Optimization of flat sheet hydrophobic membranes synthesis via supercritical CO₂ induced phase inversion for direct contact membrane distillation by using response surface methodology (RSM), *J. Supercrit. Fluids* 103 (2015) 105–114.
 - [62] D. Hou, G. Dai, J. Wang, H. Fan, L. Zhang, Z. Luan, Preparation and characterization of PVDF/nonwoven fabric flat-sheet composite membranes for desalination through direct contact membrane distillation, *Sep. Purif. Technol.* 101 (2012) 1–10.