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Fabrication of asymmetrical diffusion dialysis membrane for rapid acid recovery with high purity

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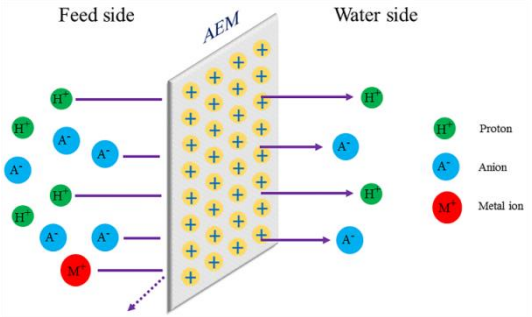
Anion exchange membranes with fast acid permeation and high retention of salts are urgently needed to increase the process efficiency of acid recovery from various industrial processes *via* diffusion dialysis, thereby greatly reducing their energy consumption and environmental impact. In this work, we have developed a novel one-step method of simultaneous crosslinking and quaternization to fabricate high-performance diffusion dialysis membranes. As an example, porous brominated poly(phenylene oxide) (BPPO) ultrafiltration membrane with a thin active layer (< 1 µm thick) was prepared and then converted to diffusion dialysis membranes by simple immersion in N,N,N′,N′-tetramethylethylenediamine (TEMED) aqueous solution. Manipulation of crosslinking and quaternization degrees by control of reaction time enabled the optimisation of the membrane performance. Apart from outstanding thermal stability and chemical resistantce in acidic envrioment, our membranes had remarkably improved performance due to the thin skin layer (<1 µm thick) and porous support, as compared to the conventional dense membranes. The optimal membrane (TPPO-4h) showed a high proton dialysis coefficient (U_{H^+}) of 0.043 m h^{-1} and high separation factor (S) of 73.8 for HCl recovery from $HCl/FeCl_2$ solution, which are 5.1 and 4 times of the corresponidng values of the commercial DF-120 membrane. In other words, the process capacity for acid recovery from the acidic waste solution can be increased from 11.3 to 57.8 L m^{-2} d^{-1}, with 3 times increase in acid purity, by replacing DF-120 with the TPPO-4h membrane. The strategy developed in this work is very promising for developing high-performance anion exchange membranes for rapid recovery of acid with high purity in many industrial processes.

1. Introduction

Rapid developments in many industries like steel processing, metal-refining, ion exchange resin regeneration, electroplating industries and mining can cause severe pollution to the environment by discharging huge amounts of acidic wastewaters.[1-7] The common methods such as neutralization, crystallization, thermal decomposition and solvent extraction require heating and addition of alkaline solution,[8] which have high energy consumption and further pollution by disposal of salts. Membrane technology using anion exchange membrane (AEM) for acid recovery *via* diffusion dialysis is an attractive tool for acid recovery and has been exploited to recover acids from waste solutions.[9] Diffusion dialysis as an attractive acid recovery method relies on the great difference in diffusivity between acids and salts and the only external power is required to circulate the solution. The separation of acid from salts is achieved by the positively charged AEM which has a tendency allowing the selective transport of anion across through the membrane, while ideally remaining impermeable to cations rather than protons because of their small volume and less positive charge,[10] as shown in Scheme 1. Compared with other common methods of dealing with the acid waste,[8] diffusion dialysis (DD) process is known as one of the most cost-effective technologies because of its unique features including lower energy consumption and lower installation and operating costs.[10-12]



Scheme 1. Schematic illustration of the diffusion dialysis process for acid/salt separation.

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However, the processing capacity and efficiency of diffusion dialysis is still quite low (e.g., 11.3 L m^{-2} d^{-1} for the commercial DF-120 membrane with acid recovery of 85-90%), thus requiring large membrane areas for industrial applications.[10] This drawback is due to the low acid permeation of AEMs used. It is noted that typical AEMs for acid recovery are dense and symmetrical in microstructure, and they are generally prepared by direct evaporation of quaternized polymer solution, exhibiting low proton permeability. For example, Luo et al. prepared a series of AEMs from hydroxylation, quaternization and sol-gel reaction of brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO), these membranes exhibited proton dialysis coefficients (U_H^+) of 0.005-0.011 m h^{-1} and separation factor (S) of 17-32 at 25 °C.[13] Wu et al. prepared a series of AEMs by quaternization and sol–gel reaction of multi-alkoxy silicon copolymer (poly(vinylbenzyl chloride-γ-methacryloxypropyltrimethoxysilane) (poly(VBC-co-γ-MPS)) in presence of poly(vinyl alcohol) (PVA).[14] The U_H^+ and S of the membranes were 0.010-0.017 m h^{-1} and 24-30, respectively. Further taking the commercial DF-120 membrane as an example, the dense membrane with thickness of 320 µm, it has a proton dialysis coefficient of only 0.009 m h^{-1} at 25 °C. To this end, the effective thickness and compactness of the diffusion dialysis membrane should be significantly reduced, and therefore, there is a pressing need for development of a new method for fabrication of high-performance membrane with greatly enhanced proton permeability and thus acid recovery efficiency.

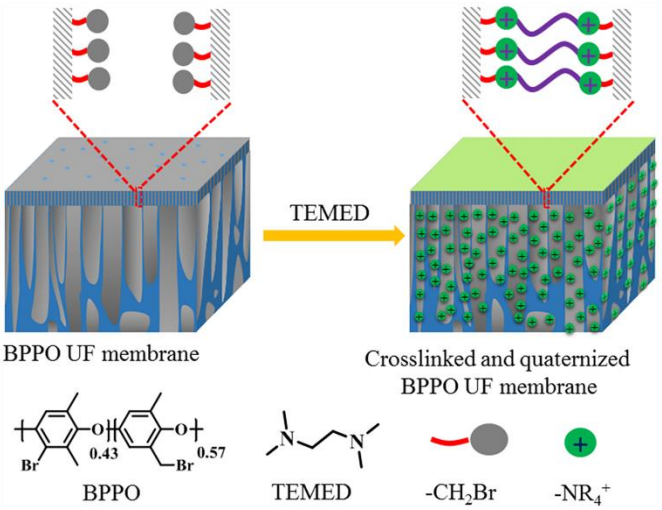
Ultrafiltration (UF) membranes are a type of porous and asymmetrical membranes prepared *via* phase inversion, having a very thin and nanoporous skin layer, a thick and macroporous supporting layer.[15] In principle, this kind of microstructure is ideal for a diffusion dialysis membrane to take advantage of thin selective layer and highly porous supporting layer for fast acid permeation. Recently, Wu et al prepared diffusion dialysis membranes by immersing brominated poly(phenylene oxide) (BPPO) UF membranes in multisilicon copolymer solution, followed by sol-gel reaction.[16] Even porous UF membranes were used as substrate, such membranes showed low U_H^+ of only 0.020–0.025 m h^{-1} and S of 28.6–45.5 at 25 °C. These results should be due to the full pore filling of the multisilicon copolymer during the preparation process.

Here we report on a new strategy for developing AEMs with remarkably improved diffusion dialysis performance by using a small-molecule diamine such as N,N,N′,N′-tetramethylethylenediamine (TEMED) to achieve simultaneous crosslinking of the active layer and quaternization . As shown in Scheme 2, brominated poly(phenylene oxide) (BPPO) was selected as starting materials for UF membrane preparation because of the excellent stability and mechanical strength, and easiness for quaternization.[17] AEMs prepared by such one-step fabrication method will have a dense active layer and a macroporous supporting layer. Consequently, high proton permeability and separation properties of the resultant membranes can be expected. The membrane structure and properties including thermal and chemical stabilities will be characterized. The enhanced acid recovery properties will be demonstrated using a mixture of HCl and $FeCl_2$ solution as the typical model waste solution in the diffusion dialysis tests.

2. Experimental

2.1. Materials

Brominated poly(phenylene oxide) (BPPO, Mw~ 60,500) was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP), N,N,N′,N′-tetramethylethylenediamine (TEMED), hydrochloric acid (HCl) and anhydrous ferrous chloride ($FeCl_2$) were purchased from Sigma-Aldrich Australia, and used without further purification. Distilled water was used throughout the experiments.



Scheme 2. Schematic diagram of the preparation of simultaneously crosslinked and quaternized BPPO ultrafiltration (TPPO) membrane.

2.2. Preparation of BPPO-based AEMs

BPPO porous membrane was firstly prepared *via* phase inversion method.[15] Specifically, BPPO was dissolved in NMP to form a 30wt% BPPO/NMP solution, in which the bubbles were removed by ultrasonication. The treated solution was dropped on a pre-cleaned glass plate and cast by a Gardco® adjustable micrometre film applicator with a stainless steel blade (Paul N. Gardner Company, Inc. USA) was used for the solution casting, whose gap was set at 250 µm. Afterwards, the cast glass was immersed in water and then the membrane was solidified in water coagulation bath after 1-2 minutes. The obtained BPPO UF membrane was washed thoroughly and stored in water before use.

BPPO-based AEMs were simply prepared by immersing BPPO UF membrane in 1 mol L^{-1} TEMED aqueous solution at 30 °C for several hours. The immersion time was varied to tailor the membrane performance. The resultant porous AEM was denoted TPPO-Xh membrane, where Xh means the immersion time of BPPO UF membrane in TEMED solution.

2.3. Membrane characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα

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source at a power of 150 W (10 kV 15 mA), a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm) The total pressure in the main vacuum chamber during analysis was typically between 10-9 and 10-8 mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed information about chemical structure and oxidation states etc., high-resolution spectra were recorded for individual peaks at 40 eV pass energy (yielding a typical peak width for polymers of 1.0). Each specimen was analysed at an emission angle of 0° as measured from the surface normal. Assuming typical values for the electron attenuation length of relevant photoelectrons, the XPS analysis depth (from which 95 % of the detected signal originates) ranges between 5 and 10 nm for a flat surface.

Surface and cross-sectional morphologies of the membranes were observed using a scanning electron microscope (FEI Nova Nano SEM microscope). The membrane samples were fixed on a SEM sample holder with double-sided carbon tape and then sputter-coated with an around 0.5nm iridium layer. For the cross-sectional morphology observation, the membrane samples was firstly immersed in distilled water for 24 h, then the water on the membrane surface was removed using a piece of Kimtech tissue paper. After that, the samples were fractured in liquid nitrogen to get clean cross sections.

Thermogravimetric analysis (TGA) was carried out by TG/DTA 6300, SII EXSTAR 6000 at a heating rate of 10°C per minute under pure argon.

The sample was fully hydrated by immersing in water for two days at different temperatures, and the weight of the wet sample (W_{wet}) was recorded by removing the water at surface to determine the water uptake (WU). Afterwards, the weight of the sample after drying (W_{dry}) at 80 °C for 12 h was also rocorded.[18] Water uptake of the sample was calculated by the the following equation:

$$\mathrm{WU} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

To analyse the ion exchange capacity (IEC), the weight of the dry sample was firstly recorded and then immersed in an aqueous NaOH solution (0.5 mol L^{-1}) at room temperature for 1 day. The treated sample was washed several times by distilled water to remove the excessive NaOH and then immersed in an aqueous NaCl solution (1 mol L^{-1}) for 1 day. The concentration of hydroxide ions released from the membrane was titrated by HCl aqueous solution using methyl orange as indicator. The IEC value was determined from the released hydroxide ions and expressed as mmol g^{-1} of the dry membrane.

The chemical stability of AEMs in acidic feed solution was determined as follows: The sample was immersed in the model acidic waste solution of HCl (~1 mol L^{-1})/(~0.2 mol L^{-1}) at 25 and 65 °C. The weight change with the immersing time was recorded to distinguish the difference and evaluate the chemical stability of AEMs.

Molecular weight cut off (MWCO) of the membranes was measured using the method similar to our previous work.[15] The membrane sample was first pre-compacted at 400 kPa for 0.5 h until it reached a constant flux. 1 g L^{-1} polyethylene glycol (PEG, molecular weight= 1, 8, 35, 100 kDa) aqueous solution was used as the feed solution, the PEG solution filtration was performed at 100 kPa and the concentrations of permeate and feed solution were measured *via* a total organic carbon analyzer (TOC-LCSH, Shimadzu, Japan). The PEG rejection (R) was calculated with the measured feed (C_f) and permeate (C_p) concentrations by the following equation:

$$\mathrm{R} = 1 - \frac{\mathrm{C_p}}{\mathrm{C_f}} \quad (2)$$

The pore size of the membrane was defined as the hydrodynamic diameter of PEG, which can be calculated from the MWCO of the membrane by the following equation:[19]

$$\mathrm{R} = 0.262\mathrm{MW}^{0.5} - 0.3\ [\text{Å}] \quad (3)$$

where MW is the lowest molecular weight of the PEG molecule at a rejection of 90% in the measurements.

Diffusion dialysis tests were performed in a cell with two chambers which were separated by an AEM with an effective area of 5.73 cm^2.[13] The feed side of the cell was filled with 140 ml HCl (~1 mol/L)/$FeCl_2$ (~0.2 mol/L) mixture solution and the permeate side with 140 mL distilled water. The membranes were conditioned for 1 day in the feed solution prior to the test and washed thoroughly with water before each test. During the diffusion test, both compartments were stirred at identical rates to minimize concentration polarization effects and the cell temperature was kept constant (25 °C, 35 °C, 45 °C, or 55 °C, respectively) using a water bath. Diffusion was allowed for 45 min and then the HCl/$FeCl_2$ solutions and water were removed from both sides of the cell. The concentration of HCl in the solutions was titrated by a standard Na_2CO_3 solution using methyl orange as indicator, while the concentration of $FeCl_2$ was determined by titration with $KMnO_4$ solution.

The separation factor (S) with respect to one species over another one is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be calculated by the following equation:

$$U = \frac{M}{At\Delta C} \quad (4)$$

where M is the amount of component transported in mole, A the effective area in square meters, t the time in h, and ΔC the logarithm average concentration between the two chambers in mole per cubic metre and defined below:

$$\Delta\mathrm{C} = \frac{(\mathrm{C_f^0} - \mathrm{C_d^t} - \mathrm{C_f^t})}{\ln[(\mathrm{C_f^0} - \mathrm{C_d^t})/\mathrm{C_f^t}]} \quad (5)$$

where $\mathrm{C_f^0}$ and $\mathrm{C_f^t}$ are the feed concentrations at time 0 and t, respectively, and $\mathrm{C_d^t}$ the dialysate concentration at time t. It should be noted that $(\mathrm{C_f^0} - \mathrm{C_d^t} - \mathrm{C_f^t})$ is not equal to zero, because water transporting through the membrane will cause volume changes in the cell chambers during the experiment.[20]

3. Results and discussion

3.1. Surface elemental composition and membrane morphology

As described above, porous BPPO ultrafiltration membrane was simultaneously crosslinked and quaternized by TEMED with

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di-tertiary amine groups as cross-linker and quaternization agent. Due to highly reactive nucleophilic substitution reaction between tertiary amine groups ($-N(CH_3)_3$) in TEMED and benzyl bromide groups ($-CH_2Br$) in BPPO UF membrane matrix, the BPPO UF membrane would be effectively crosslinked to reduce pore sizes of the active layer and ensure the necessary separation properties of membrane. Simultaneously, the resulting quaternary ammonium ($-N^+(CH_3)_3$) groups determining the ion transport were introduced into BPPO UF membrane matrix. Consequently, crosslinked TPPO AEMs were obtained and expected to possess high proton permeability and separation properties in the acid recovery by diffusion dialysis.

Table 1. Weight percentage and visual observation of BPPO and TPPO membranes after immersion in NMP under stirring at 25 °C for 24 h.

Membrane	Weight percentage (%)	Visual observation
BPPO	-	dissolved
TPPO-1h	-	gel-like
TPPO-2h	-	gel-like
TPPO-3h	-	debris
TPPO-4h	99.0	stable
TPPO-5h	98.5	stable

As shown in Table 1, it was found that BPPO porous membrane was completely dissolved in NMP within a few seconds. After crosslinking by TEMED, TPPO became insoluble in NMP. The crosslinking degree significantly affected the mechanical properties of the resultant TPPO membranes. When the crosslinking reaction was conducted for 1h or 2 h, gel-like membranes with lower crosslinking degree (TPPO-1h and TPPO-2h) were formed after immersing in NMP for 24h under stirring. As the crosslinking time was increased to 3h, the resulting membrane (TPPO-3h) became firm. By contrast, TPPO-4h and TPPO-5h remained stable in NMP and their remaining weights after immersing in NMP for 24h under stirring were 98.1% and 97.5%, respectively. These results indicate that the TPPO membranes with a high crosslinking degree show good solvent resistance.

XPS was used to investigate the chemical composition at the top surface of the TPPO UF membrane. Figure 1 and 2 show the survey spectra and high resolution spectra of N1s region of BPPO and TQPPO-4h membranes, respectively. For survey spectra, the expected elements such as O1s, N1s, C1s and Br3d can be observed. From BPPO to TPPO-4h membrane, the N element intensity increases while Br element intensity decreases. As shown in Table 2, from BPPO to TPPO-4h membrane, the atomic percentages of N and Br elements increase from 4.48% to 7.54% and decrease from 4.69% to 0.82%, respectively. This is easily understood given the conversion of benzyl bromide groups to quaternary ammonium groups resulting from the nucleophilic substitution reaction. For high resolution spectra of N1s region giving more detail, the newly formed peak at 402.4ev[21] from BPPO to TPPO-4h membrane confirms the successful introduction of quaternary ammonium groups in TPPO membranes.

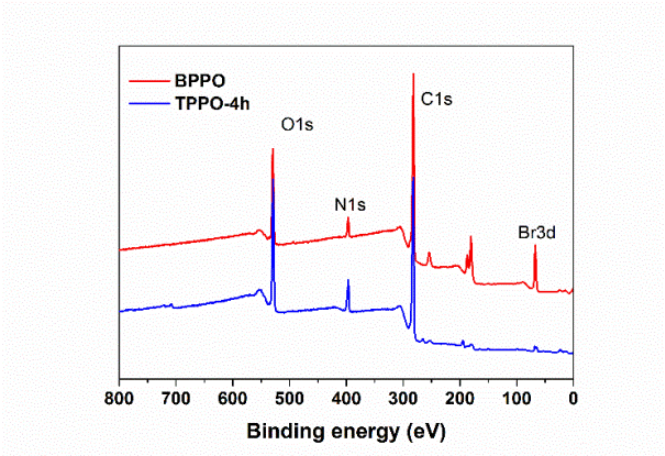

Figure 1. Survey spectra of BPPO and TPPO-4h membranes active layers.

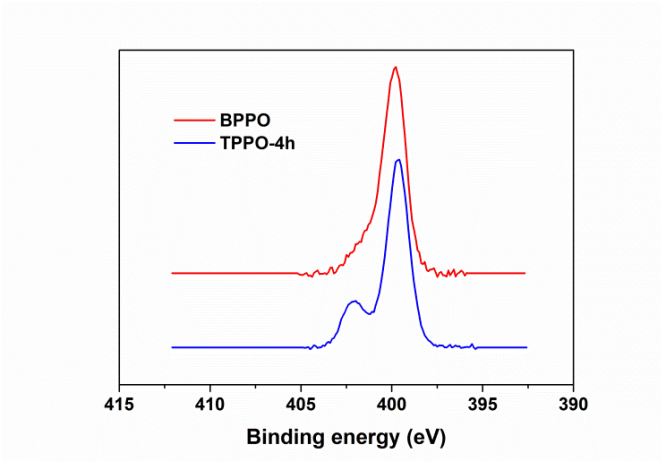

Figure 2. High-resolution spectra of N1s region of BPPO and TPPO-4h membranes.

Table 2. Atomic percentage calculated from XPS peak area for BPPO and TPPO membranes

Atomic percentage (%)	BPPO	TPPO-4h
N	4.48	7.54
C	75.82	70.44
O	14.39	19.33
Br	4.69	0.82

SEM images of BPPO, TPPO-2h, TPPO-4h and TPPO-5h membranes are shown in Figures 3-5. Generally, BPPO exhibits a typical asymmetrical microstructure with a thin nanoporous skin layer and a finger-like macroporous supporting layer. There are abundant uniformly distributed nanopores on the top surface (Figure 3a), asymmetrically porous channels on the cross section of the skin layer (Figure 4a), and macropores with a pore size of sub-micron on the bottom surface (Figure 5a). The microstructure of the membrane is affected by the crosslinking effect after immersion of BPPO UF membrane in TEMED solution. From BPPO membrane to TPPO-2h membrane, the size and density of the pores at the top and bottom surfaces (Figure 3 and 5) decrease, attributed to the crosslinking effect. The molecular weight cut off (MWCO) of BPPO and the selected TPPO-4h membranes were tested to

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evaluate their pore size at the skin layer. Specifically, BPPO has a MWCO of about 22 kDa and its average pore size is 7.6 nm, after crosslinking treatment, TPPO-4h has a MWCO of about 1 kDa and its pore size at the top surface is about 1.4 nm. The change in surface micro-structure is expected to improve separation properties of the resultant TPPO membranes because of the avoidance of the ion leakage. However, there is no obvious change in cross-sectional morphology of the membrane from BPPO to TPPO membranes even when the immersion time is extended to as long as 5 h (Figure 4), while only a slight increase in the thickness of the skin layer (from 830 to 870 nm) can be observed for TPPO membranes with increasing immersion time in TEMED solution due to the enhanced crosslinking effect. Compared with the conventional dense membrane, whose thickness are always dozens to hundreds micrometers, the thin skin layer of the crosslinked UF membrane will greatly promote the membrane transport properties.

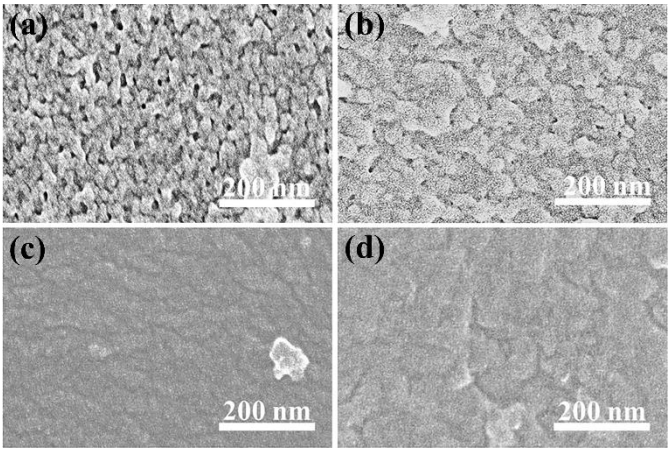

Figure 3. The top-surface SEM images of (a) BPPO, (b) TPPO-2h, (c) TPP0-4h, and (d) TPPO-5h membranes.

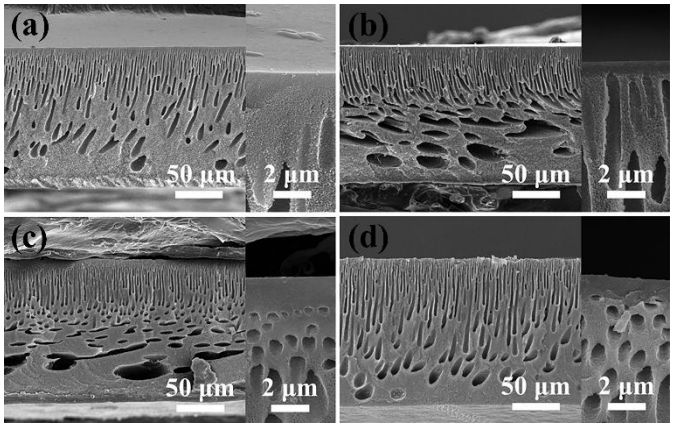

Figure 4. The cross-sectional SEM images of (a) BPPO, (b) TPPO-2h, (c) TPP0-4h, and (d) TPPO-5h membranes.

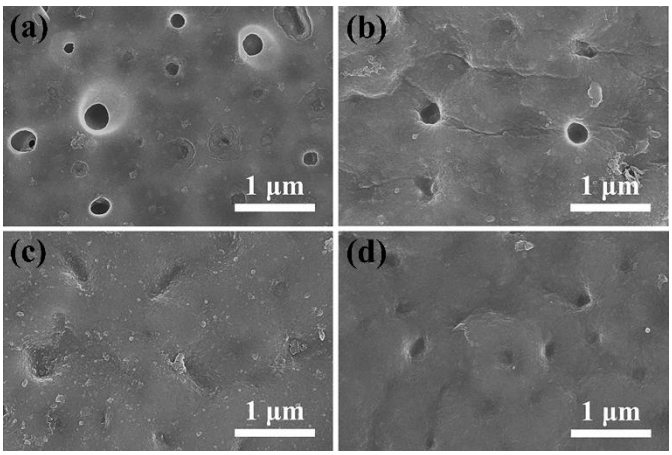

Figure 5. The bottom-surface SEM images of (a) BPPO, (b) TPPO-2h, (c) TPP0-4h, and (d) TPPO-5h membranes.

3.2. Ion exchange capacity

Quaternary ammonium groups, as the ion exchange groups of TPPO membranes, will provide the membrane with ion transport sites. As BPPO UF membrane was immersed in 2 mol L^{-1} TEMED aqueous solution at 30 ^{o}C to conduct the quaternization process, the immersion time would directly determine the density of quaternary ammonium groups (IEC), and consequently diffusion dialysis performance of the resultant TPPO membrane. As shown in Figure 6, IEC of the pristine BPPO is equal to 0 (<0.02 mmol g^{-1}) due to the absence of anion exchange groups, after immersing in TEMED solution, IEC of TPPO-1h to TPPO-4h membranes increases from 0.51 to 1.43 mmol g^{-1}, attributed to the increasing amount of quaternary ammonium groups formed via reaction between –CH2Br and TEMED. After that, IEC value remains almost constant due to the full conversion from -CH_2Br groups to quaternary amine groups.

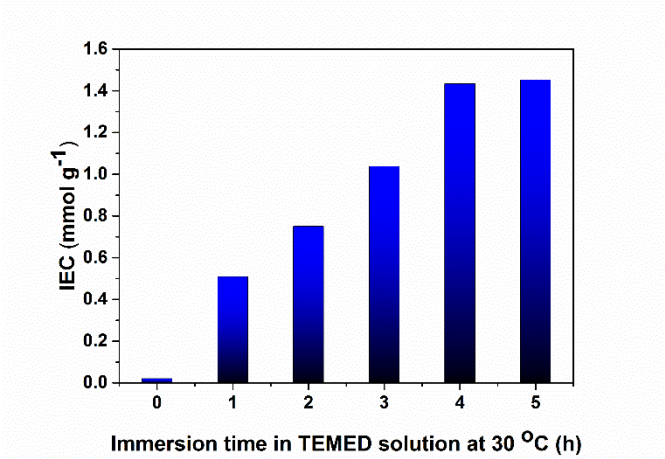

Figure 6. Ion exchange capacity (IEC) values of BPPO and TPPO membranes.

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3.3. Water uptake

Figure 7 shows the water uptake (WU) of the porous BPPO and TPPO membranes tested at 25°C and 65 °C. WU values of the pristine BPPO ultrafiltration membrane are 151% at 25 °C and 163% at 65 °C. By contrast, WU value of the dense BPPO membrane is almost 0 at 25 and 65 °C. This difference should be due to the porous structure of ultrafiltration membrane for water adsorption. TPPO membranes show higher water uptake than BPPO ultrafiltration membrane because of high water adsorption by the hydrophilic quaternary ammonium groups. WU values of TPPO membrane increase from 171% to 336% at 25 °C due to the increasing amount of hydrophilic quaternary ammonium groups. It is well known that WU value of ion exchange membrane would increase with increasing temperature because of the higher temperature leads to higher swelling ratio and free space in membrane matrix.[22] However, there is no obvious change in WU of TPPO membranes observed even when temperature is increased from 25 to 65 °C. This can be explained by the fact that the crosslinking treatment by TEMED lowers the swelling ratio of the TPPO membranes at high temperatures.

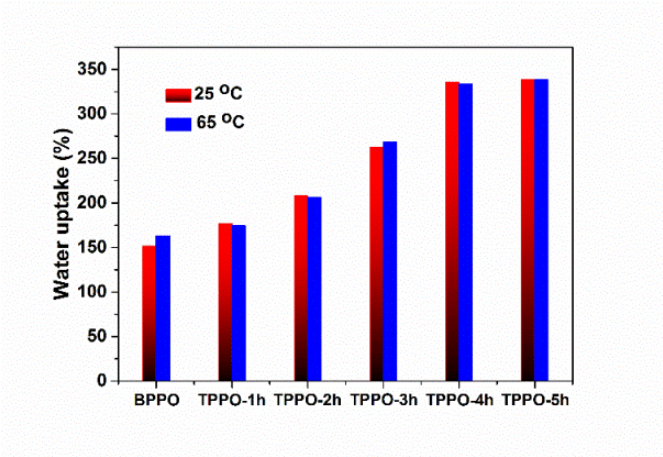

Figure 7. Water uptake (WU) values of the porous BPPO and TPPO membranes at 25 and 65 °C

3.4. Diffusion dialysis performance

Diffusion dialysis performance of TPPO membranes was investigated to evaluate their potential for acid recovery. The mixture of HCl and $FeCl_2$ aqueous solution was used as the model acidic waste solution. Figure 8 shows proton dialysis coefficient (U_{H^+}) and separation factor (S) of TPPO membranes at 25 °C. From TPPO-1h to TPPO-5h membrane, U_{H^+} and S values both increase from 0.009 to 0.043 m h^{-1} and 46.6 to 73.8, respectively. As discussed above, TPPO membranes were simultaneously crosslinked and quaternized by TEMED, the resultant membranes prepared with longer immersion time would possess both higher IEC and crosslinking degree. The former governs ion transport in membrane matrix while the latter determines salt rejection. Hence, the trend of proton dialysis coefficient and separation factor is easily understood.

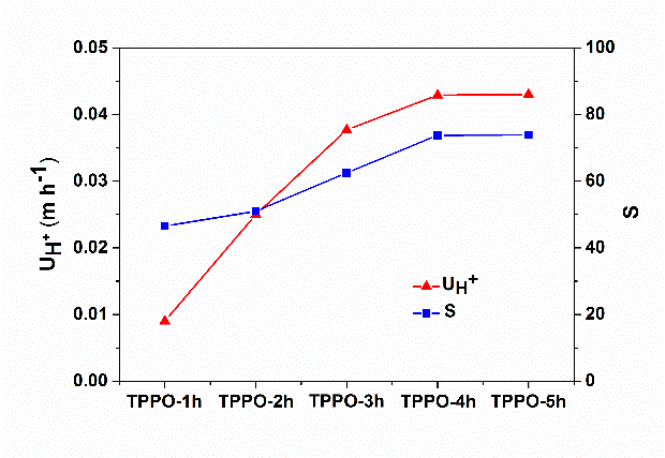

Figure 8. Proton dialysis coefficient (U_{H^+}) and separation factor (S) of TPPO membranes at 25 °C.

Table 3 summarizes ion exchange capacity (IEC), proton dialysis coefficient (U_{H^+}) and separation factor (S) of TPPO membrane and some reported membranes at 25 °C using HCl/$FeCl_2$ solution as model acidic waste solution. Compared with AEMs prepared by immersing BPPO UF membrane in multisilicon copolymer solution followed by sol-gel reaction,[16] which showed low U_{H^+} of only 0.020–0.025 m h^{-1} and S of only 28.6–45.5 at 25 °C, TPPO-4h membrane exhibits up to 115.0% increase in proton permeability and 158.0% increase in separation factor, indicating the superiority of the *in-situ* treatment, and it would remain the micro-structure of UF membrane substrate and take advantage of its unique properties including extremely small effective thickness and high porosity. Compared with the diffusion dialysis performance of some reported dense AEMs,[13, 14, 23-27] TPPO-4h also shows a significant improvement. Further compared with the commercial DF-120 membrane, whose process capacity for acid recovery is about 11.3 L m^{-2} d^{-1}, TPPO-4h and TPPO-5h show 4.1 and 3.0 times increase in proton dialysis coefficient and separation factor, respectively. This should be due to the reduction in thickness (320 µm vs 1 µm) and compactness (dense vs porous), when dense commercial DF-120 membrane is compared with porous TPPO membrane. In other words, if commercial DF-120 membrane is replaced with TPPO-4h membrane, the acid recovery capacity is expected to increase from 11.3 to 57.8 L m^{-2} d^{-1}, with 3 times increase in acid purity, suggesting the great potential for rapid recovery of acid with high purity.

TPPO-4h was selected to perform diffusion dialysis experiments at different temperatures. The results including proton permeability (U_{H^+}) and separation factor (*S*) between proton permeability and ferrous ion at different temperatures are presented in Figure 9. With increasing temperature from 25 to 55 °C, U_{H^+} of TPPO-4h membrane increases from 0.043 to 0.063 m h^{-1}; this is because of enhanced ion transport rate at higher temperature.[13] However, its separation factor slightly increases from 73.8 to 78.2 when the temperature increases from 25 to 35 °C, but decreases from 78.2 to 41.1 when temperature increases from 35 to 55 °C. In other words, the

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enhancement in Fe^{2+} ion transport at higher temperature is more significant for that in proton ions at high temperature.[13] However, the separation factor of 50.6 at 45 °C and 41.1 at 55 °C is still high enough for diffusion dialysis application. Further considering the corresponding high U_{H^+} of 0.058 m h^{-1} at 45 °C and 0.063 m h^{-1} at 55 °C, the TPPO-4h membrane should have excellent diffusion dialysis performance at different temperatures. In addition, the one-step post-functionalization of pre-formed ultrafiltration membrane method used here greatly simplifies the preparation process and shortens the reaction time as compared with the method for the dense membrane, showing outstanding economic and environmental benefits.

Table 3. Ion exchange capacity (IEC), proton dialysis coefficient (U_{H^+}) and separation factor (S) of TPPO-4h and some reported membranes at 25 °C using HCl/$FeCl_2$ solution as model acidic waste solution.

Membrane	Compactness	IEC (mmol g^{-1})	U_{H^+} (10^{-3} m h^{-1})	S	Ref.
TPPO-4h membrane	porous	1.43	43	73.8	This work
BPPO UF membranes immersed in multisilicon copolymer solution	porous	1.75-2.45	20–25	28.6–45.5	[16]
DF-120 commercial membrane	dense	1.96	9	18.5	-
Quaternized PPO based hybrid membranes	dense	1.7–2.2	5-11	17.0-32.0	[13]
PVA and multi-alkoxy silicon copolymer blending membranes	dense	0.34 - 0.76	10-17	24.0-30.1	[14]
PVA treated with alkoxysilanes membranes	dense	0.52-1.01	8-10	15.9-21.0	[23]
Quaternized poly(VBC-co-γ-MPS) membranes	dense	0.6–0.9	24-43	22-26	[24]
Quaternized Bionic multisilicon copolymers	dense	0.46-1.25	7.2-7.5	25.9-42.8	[25]
Quaternized blending of PPO and PVA membranes	dense	1.22-1.92	21-49	26-39	[26]
Quaternized aromatic amine based hybrid PVA membranes	dense	0.65-1.12	17.2-25.2	14–21	[27]

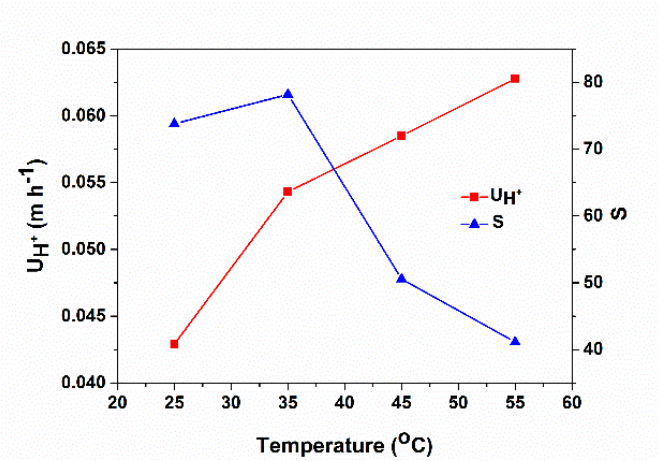

Figure 9. Proton dialysis coefficient (U_{H^+}) and separation factor (S) of TPPO-4h membrane at different temperatures.

3.5. Thermal and chemical stabilities

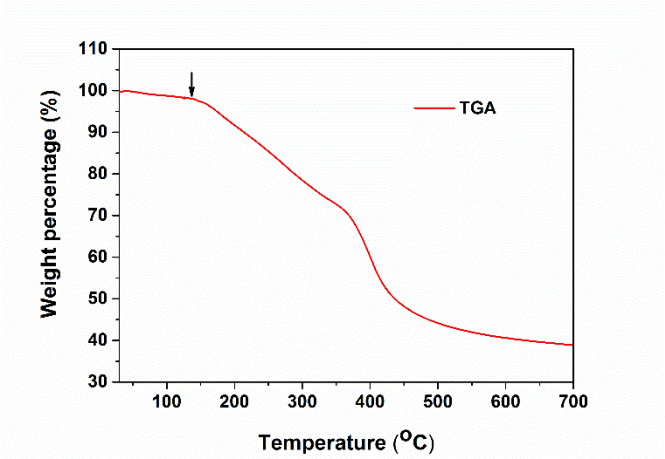

Figure 10. TGA curve of TPPO-4h membrane.

Apart from high proton permeability and superior rejection of salts, the stability of AEMs is also crucial for industrial diffusion dialysis applications, including thermal stability and high acidic resistance.[12, 20] TPPO-4h was selected for the stability investigation among TPPO membranes.

The thermal stability of the TPPO membranes was evaluated by TGA under an argon atmosphere and the TPPO-4h was selected. From Figure 10, the decomposition onset temperature of TPPO-4h is around ~150 °C, demonstrating the excellent thermal stability of TPPO membranes. Moreover, the first weight loss starts at around 150 °C due to the decomposition of quaternary ammonium groups of the TPPO membranes,[28] while the second weight loss at ~360 °C is due to the degradation of the polymer backbone.[22]

For the investigation of the chemical stability of the TPPO membrane, TPPO-4h was immersed in HCl/$FeCl_2$ feed solution at 25 and 65 °C for 7 days, the weight change of the membrane was recorded at the increasing immersion time. As shown in Figure 11, the TPPO-4h membrane remains stable and shows no weight loss observed even after being immersed in hot acidic

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feed solution for as long as 7 days, suggesting the excellent chemical stability of the resultant TPPO membranes.

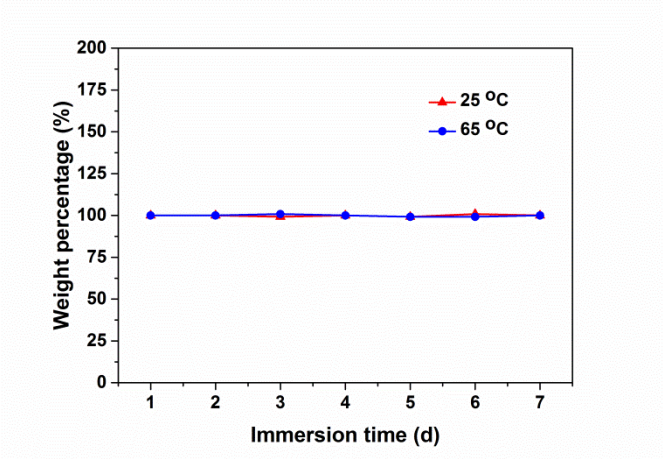

Figure 11. The weight percentage of the TPPO-4h membranes after immersing in aqueous HCl/$FeCl_2$ solution at 25 °C and 65 °C for increasing lengths of time.

Conclusion

BPPO-based diffusion dialysis membranes (TPPO membranes) have been successfully prepared by immersing pre-formed BPPO ultrafiltration membranes in aqueous TEMED solution for simultaneous crosslinking and quaternization. The resultant membranes are composed of a thin crosslinked skin layer and a thick macroporous supporting layer, and their ion exchange capacity, water uptake, proton diffusion coefficient and separation factor increased with increasing the immersion time. Because of asymmetric microstructure, the TPPO membranes show remarkably better diffusion dialysis performance than the previously reported membranes and the commercial DF-120 membrane; the membranes also show excellent thermal and chemical stabilities. Therefore, the membranes and their fabrication method developed here hold great potential for commercial development of high-efficiency diffusion dialysis technology for fast acid recovery from industrial processes.

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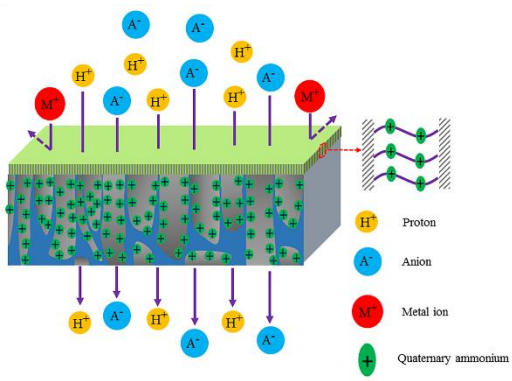

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