Asymmetrically porous anion exchange membranes with an ultrathin selective layer for rapid acid recovery

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Abstract

Diffusion dialysis for acid recovery from acidic waste solution suffers from the low process capacity due to low proton permeability of current dense anion exchange membranes. In this work, asymmetrically porous ultrafiltration membranes with a thin skin layer (e.g., <1 micrometer) were converted to diffusion dialysis membranes with a hierarchically porous structure after in situ crosslinking and quaternization. Except for good thermal and chemical stabilities, the resulting membranes exhibited an acid permeability coefficient as high as 0.041-0.062 m h⁻¹ and a separation factor of 30.4-84.4, which are 4.1-6.3 times and 0.6-3.6 times higher than the commercial DF-120 membrane, respectively. The acid recovery capacity can be enhanced from 11.3 to 82.4 L m⁻² d⁻¹, with a 64% increase in acid purity when our new membrane was used to replace the commercial DF-120 membrane. Moreover, these results are also superior to most of the reported membranes. Therefore, the excellent performance and simple preparation process endow our new diffusion dialysis membranes with great potential for high-efficiency industrial acid recovery applications.

Keywords: diffusion dialysis, ultrathin, asymmetrically porous, acid recovery, acidic wastewater
1. Introduction

One of the most pervasive problems afflicting environment is the wastewater discharge during industrial production [1, 2]. Large amount of acidic waste solutions produced from industrial production cause serious environmental problems and waste resources [3-7]. The common acid waste treatments such as neutralization, crystallization, thermal decomposition and solvent extraction suffer from high energy consumption and further pollution by disposal of salt by-products [8]. Acid recovery via diffusion dialysis employing anion exchange membranes has been applied for many years due to its operational simplicity, compatibility with either small or large plating plants and economic advantages in terms of capital investment and operating costs [9-11]. It relies on the difference in the diffusivity between acid and salt in an anion exchange membrane due to the difference in steric hindrance and electrostatic repulsive force, and therefore acid can be separated from salt by diffusion dialysis [12].

As the key component in diffusion dialysis, the anion exchange membrane should have high acid permeability and salt rejection, and long-term stability including high chemical and thermal stabilities to satisfy the demand of practical production. To date, most of the anion exchange membranes used in diffusion dialysis are dense membranes. One type of them are homogenous and symmetrical membranes, prepared by the direct evaporation of the polymer solution to form the homogeneous membranes [13]. However, they are thick (several tens or hundreds of microns) and dense in microstructure and show low ion permeability leading to low process capacity and efficiency. For instance, a commercial dense membrane DF-120 with a thickness of 320 micrometers has the proton (H\(^+\)) dialysis coefficient (U\(_{H^+}\)) of only 0.0085 m h\(^{-1}\) at 25°C. Even various modifications have been conducted to improve the diffusion dialysis performance of the symmetrically dense anion exchange membranes, the improvement remains unsatisfying given its dense microstructure [14-24]. Another type of dense anion exchange membranes for diffusion dialysis are asymmetric membranes, they can prepared from the
copolymerization of monomers within the pores of pre-formed porous membranes substrate [25-28] or blending of the different polymer or additive components [29, 30]. Recently, the method of electrospinning of quaternized polymer nanofibers, followed by solvent fumigation and hot-press has been utilized to fabricate asymmetrically dense anion exchange membrane [31]. Even though good diffusion dialysis performance can be achieved for asymmetric anion exchange membrane, they are always complex in fabrication process and their large-scale production is therefore limited.

Ultrafiltration membranes are typical asymmetric and porous membranes simply prepared via nonsolvent-induced phase inversion [32], and are widely used in water treatment [33-35]. Typically, they have a thin nanoporous skin layer with a thickness of sub-micrometer and a thick and macroporous supporting layer. Considering the hierarchical porous structure of ultrafiltration membrane, the high acid permeability of ultrafiltration membranes can be expected after the modification to block the pores at the top surface and introduce the positively charged groups into the membrane matrix. Since ultrafiltration membranes can be conveniently prepared via the phase inversion technique [32], the conversion of ultrafiltration membranes is a simple and effective method for the large-scale production of high-performance diffusion dialysis membranes. In our previous work, we have demonstrated that asymmetrically porous anion exchange membranes prepared from ultrafiltration membranes after crosslinking and quaternazation treatment show significantly high proton permeablitly for acid recovery by diffusion dialysis [36, 37]. Specifially, anion exchange membranes prepared from ultrafiltration membrane by the simultaneously crosslinking and quaternization with \(N,N,N',N'-\)tetramethylethylenediamine (TEMED) showed highest acid permeability coefficient (\(U_{H^+}\)) of 0.043 m h\(^{-1}\) [37]. Moreover, anion exchange membranes prepared from ultrafiltration membrane by crosslinking with polyethyleneimine (PEI) and subsequent quaternization with trimethylamine (TMA) showed significantly increased \(U_{H^+}\) of 0.063 m h\(^{-1}\), unfortunately, their
separation factor is quite lower because of the usage of the polymer crosslinker, which is inadequate for fully crosslinking due to the high steric hindrance [36]. It is noted that the newly reported work on the direct conversion of ultrafiltration membrane into diffusion dialysis membrane is insufficient, it is still essential to optimize the functionalization process, such as the investigation of the effect of the crosslinker type to obtain anion exchange membranes with optimal diffusion dialysis performance.

Rather than the polymer crosslinker, in this work, small molecule compound 1, 4-butanediamine (BTDA) was used as crosslinker for the in situ modification of ultrafiltration membrane. Specifically, brominated poly(phenylene oxide) (BPPO) was selected as a starting material for ultrafiltration membrane preparation for its superior stability and mechanical strength, and the ease of quaternization [38]. Because of the presence of the abundant nanopores at the top layer, BPPO ultrafiltration membrane was firstly in situ crosslinked by BTDA to greatly reduce the nanopore sizes and block the permeation of large ions while ensuring the necessary mechanical properties. The crosslinked membrane was then quaternized by trimethylamine (TMA) to yield quaternary ammonium groups for selective ion transport. Considering the weaker steric hindrance of BTDA as compared with polymer PEI, the improvement in separation factor and mechanical properties can be expected due to the enhancement in crosslinking degree and compactness of the membranes. Afterwards, the functionalization process and the chemical structure of the resultant membranes will be characterized and discussed in detail. Moreover, the membrane properties especially diffusion dialysis performance will be also investigated.

2. Materials and Methods

2.1. Materials

Brominated poly(phenylene oxide) (BPPO, Mw~ 60,500) with a benzyl substitution ratio of 0.57 was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP), 1,
4-butanediamine (BTDA), trimethylamine (TMA), hydrochloric acid (HCl), anhydrous ferrous chloride (FeCl2), sodium carbonate (Na2CO3) and potassium permanganate (KMnO4) were purchased from Sigma-Aldrich, Australia, and used without further purification. Distilled water was used throughout the experiments.

**2.2. Preparation of BPPO ultrafiltration membrane**

The flat sheet BPPO ultrafiltration membranes used in this study were prepared via phase inversion according to our previous work [39]. In brief, a given quantity of BPPO was dissolved in NMP at room temperature to obtain a 30wt% BPPO/NMP casting solution. The polymer solution was ultrasonically treated to allow air bubbles to escape. The resulting polymer casting solution was uniformly spread onto a glass plate using a Gardco® adjustable micro-meter film applicator with a stainless steel blade (Paul N. Gardner Company, Inc. USA) with a selected gap of 250 μm. The glass plate with the casting solution was immediately immersed into a distilled water bath at room temperature; the membrane soon precipitated on the glass plate in several seconds. The membrane was thoroughly rinsed and then immersed in distilled water prior to characterization and performance test.

**2.3. Preparation of crosslinked and quaternized anion exchange membrane**

As shown in Scheme 1, The BPPO ultrafiltration membranes was simply immersed in 1mol L⁻¹ BTDA aqueous solution at 40 °C for several hours to control the crosslinking degree of the resultant crosslinked BPPO membranes (namely as BBPPO membranes). After washed thoroughly with water, the membranes were then immersed in 1 mol L⁻¹ TMA aqueous solution at 60 °C for 6 h to make sure the fully quaternization. The final quaternized and crosslinked BPPO ultrafiltration anion exchange membranes treated by BTDA and TMA were designated as BTPPO-xh membranes, where xh is the immersion time in BTDA solution.

**2.4. Characterization**

**2.4.1. Scanning electron microscopy (SEM) analysis**
Scanning electron microscopy was undertaken with a Nova NanoSEM 450 FESEM, FEI, USA.). 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.

2.4.2. X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα 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, oxidation states etc., and high resolution spectra were recorded from 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

2.4.3. Thermogravimetric analysis (TGA)

Thermal stability of the membrane sample was performed on a SII EXSTAR 6000 TG/DTA 6300 under argon flow and with a heating rate of 10 °C min⁻¹. 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.

2.4.4. Water uptake
Water uptake was calculated by taking the difference between the wet weight ($W_{\text{wet}}$) and dry weight ($W_{\text{dry}}$) of the membrane samples [40]. These samples were equilibrated with distilled water at 25 or 65 °C in 2 days. The samples were then removed, dried with tissue papers, and then weighed. These membranes were then dried at an oven at 100 °C for 24 h to get a constant dry weight. The water uptake of all membrane samples was calculated according to Eq. (1) as follow:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$  \hspace{1cm} (1)

**2.4.5. Contact angle**

The wettability of the membrane was analyzed by a contact angle goniometer (Dataphysics OCA15, Dataphysics, Germany). The membrane samples were firstly immersed in distilled water for 24 h, and the membrane was then cut into the desired shape. The water on the surface of the membrane was removed by the filter carefully for contact angle measurement.

**2.4.5. Ion exchange capacity (IEC)**

The ion exchange capacity (IEC) was measured using the Mohr method. The membrane was firstly dried and weighted and then soaked in 0.5 mol L$^{-1}$ NaOH aqueous solution at room temperature for 12 h to replace Br$^-$ ions with OH$^-$ ions. After thoroughly washed with distilled water, the sample was soaked in 1 mol L$^{-1}$ NaCl aqueous solution for 1 day to release OH$^-$ ions from membrane matrix. The concentration of OH$^-$ released from the membrane was determined by titration with 0.05 mol L$^{-1}$ HCl aqueous solution using methyl orange as indicator, the resultant IEC value was calculated from the released OH$^-$ ions and expressed as mmol g$^{-1}$ of the dry membrane.

**2.4.6. Chemical stability**

For investigation of the chemical stability of the prepared membranes in an acidic environment, the membrane samples were immersed in an aqueous HCl (~1 mol/L)/FeCl$_2$ (~0.2 mol/L) mixture solution for different lengths of time at 25 and 65 °C, which is a harsh hot and
acidic environment for the membrane used in diffusion dialysis. The change in weight percentage and diffusion dialysis performance by the acidic treatment was determined to evaluate the membrane chemical stability.

2.4.7. Diffusion dialysis tests

Diffusion dialysis runs were performed in a cell with two chambers, which were separated by a membrane with an effective area of 5.73 cm \(^{14}\). Prior to the test, the membranes were conditioned for 1 day in the feed solution and washed thoroughly by water for 3-4 days until pH neuter was achieved. Then the membrane was fixed between two chambers with top surface facing feed solution. The feed side of the cell was filled with 140 ml of HCl (~1 mol/L)/FeCl\(_2\) (~0.2 mol/L) mixture solution and the permeate side with 140 mL distilled water. During the diffusion test, both compartments were stirred at identical rates to minimize concentration polarization effects and the cell temperature was kept constant at 25 \(^\circ\)C by 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 determined by acid–base titration with a standard Na\(_2\)CO\(_3\) (0.05 mol L\(^{-1}\)) solution using methyl orange as indicator, while the concentration of FeCl\(_2\) was determined by the oxidation titration with purple KMnO\(_4\) solution (0.001 mol L\(^{-1}\)) as simultaneous oxidizing agent and indicator.

The separation factor with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be calculated according to Eq. (2) as follow:

\[
U = \frac{M}{At\Delta C} \tag{2}
\]

where M is the amount of component transported in moles, A the effective area in m\(^2\), t the time in h, and \(\Delta C\) the logarithm average concentration between the two chambers in moles m\(^{-3}\) and defined according to Eq. (3) as follows:

\[
\Delta C = \frac{(c^{f}_0 - c^{f}_d - c^{d}_f)}{\ln[(c^{f}_0 - c^{d}_d)/(c^{f}_d)]} \tag{3}
\]
where \( C_f^0 \) and \( C_f^t \) are the feed concentrations at time 0 and t, respectively, and \( C_d^t \) the dialysate concentration at time t. It should be noted that \( (C_f^0 - C_d^t - C_f^t) \) is not equal to zero, because water transport through the membrane will cause volume changes in the cell chambers during the experiment [41].

3. Results and Discussion

3.1. Chemical structure

The membranes based on BPPO ultrafiltration membrane with different treatment procedures were prepared and their proton dialysis coefficients \( (U_{H^+}) \) at 25 °C were tested. As shown in Table 1, for BPPO ultrafiltration membrane treated with TMA (2#) only, it suffered from serious swelling and its mechanical strength was too low for testing [36]. Moreover, the pristine BPPO membrane (1#) and BBPPO ultrafiltration membrane only treated with BTDA (3#) showed no proton permeability as there were no ion exchange groups in the membrane matrix (See XPS spectra in Fig. 1). By contrast, BTPPO ultrafiltration membrane treated with BTDA and TMA (4#) in turn showed proton dialysis coefficients of 0.062 m h\(^{-1}\) and separation factor of 30.4. These results demonstrate the necessity of BTDA and TMA treatment for BPPO ultrafiltration membrane modification for DD application.

The functionalization process as well as the chemical composition at the top surface were determined using the XPS technique. Fig. 1 shows the survey spectra and high resolution spectrum of the pristine BPPO, BBPPO-4h and BTPPO-4h membranes, respectively. The peaks of O1s, N1s, C1s and Br3d are clearly presented in Fig. 1(a). From BPPO to BBPPO and BTPPO, the intensity of N element increases while that of Br element decreases. As shown in Table 2, from BPPO to BBPPO and BTPPO membranes, the atomic percentage of N and Br element will increase from 4.48% to 5.08% and 7.54% and decrease from 4.69% to 2.48% and
2.20%, respectively, due to the conversion of -CH$_2$Br groups to amine groups during the functionalization process. The presence of newly formed quaternary ammonium group is confirmed by the peak at 402.1 eV [42] in the high-resolution spectrum (Fig. 1(b)) for BTPPO rather than BPPO and BBPPO membranes. That is the reason why BPPO and BBPPO membranes showed no proton permeability in our preliminary work, attributing to the absence of the anion exchange groups for ion transfer. These results confirm the successful functionalization process and the introduction of quaternary ammonium groups as anion exchange groups.

3.2. Membrane morphology

SEM images of BPPO, BBPPO and BTPPO membranes are investigated. As shown in Fig. 2, BPPO ultrafiltration membrane exhibits a typical asymmetrical microstructure with a thin nanoporous active layer, macroporous supporting layer with asymmetric porous channels on the cross section, and macroporous bottom surface. The crosslinking effect of BTDA as crosslinker significantly affects the micro-structure of the BBPPO. For the top surface, the pores decrease in size obviously resulting from the crosslinking treatment from BPPO to BBPPO-4h and then become unobservable from BBPPO-4h to BBPPO-5h with the increasing crosslinking degree. The change in the morphologies of the bottom surface of BBPPO are similar to that of the top surface, that is, the pores at the bottom surface also become unobservable after the crosslinking treatment. However, there is no obvious change in cross section including active layer can be observed from BPPO to BBPPO membranes.

From BBPPO to BTPPO after further reacting with TMA, the pores at the top surface of BTPPO membrane disappear due to the swelling effect of the hydrophilic quaternary ammonium groups. Beyond that, no change can be observed for the morphology of BTPPO membrane (Fig. 3) as compared with BBPPO membrane. These results suggest that the unique micro-structure of the ultrafiltration membrane can be maximum remained for BTPPO
membranes except blocking the pores at their surfaces. Moreover, the thickness of the skin layer as the effective thickness of BTPPO ultrafiltration membranes is about 0.85 µm. By contrast, the conventional dense membrane always show dozens to hundreds µm in thickness, the great decrease in low thickness and obviously porous structure can be expected to greatly facilitate the proton permeability of the membrane.

### 3.3. Ion exchange capacity

It is well known that electrochemical properties of anion exchange membrane are dependent on the amount of anion exchange groups that directly control ion transport in the membrane matrix. In our work, BPPO ultrafiltration membranes were firstly crosslinked by immersing in BTDA solution with different time along with the consumption of partial –CH₂Br groups and then fully quaternized by TMA solution to convert the residual –CH₂Br groups to quaternary ammonium groups to obtain the final crosslinked and quaternized BTPPO membranes. Distinctly, the above-mentioned first step determines not only the crosslinking degree but also the density of quaternary ammonium groups of BTPPO membranes, which are the key to the separation properties and proton permeability of the membrane for diffusion dialysis, respectively.

The membrane properties including ion exchange capacity, water uptake, and diffusion dialysis performance were investigated. From BTPPO-1h to BTPPO-4h membrane with the increasing immersion time in BTDA, the ion exchange capacity (IEC) value, a measure of the charge density, decreases from 1.45 to 1.01 mmol g⁻¹ (Fig. 4), which was attributed to the decrease in the amount of –CH₂Br groups left for quaternization. From BTPPO-4h to BTPPO-5h membrane with even a longer immersion time in BTDA solution, IEC value remained unchanged. In other words, BPPO ultrafiltration membrane was already fully crosslinked after immersed in BTDA solution for 4 h.

### 3.4. Water uptake and contact angle
Basically, the water uptake of ion exchange membranes is strongly dependent upon IEC and also related to the temperature [43]. Fig. 5 shows the water uptake and contact angle values of BPPT membranes. As expected, the water uptake value of the membrane shows a similar trend with that of IEC. Specifically, from BPPO-1h to BPPO-4h membrane, the water uptake value at 25 °C decreases from 333.3% to 223.3%; it then remains about the same from BPPO-4h to BPPO-5h membrane. It is easily understood that the hydrogen bond interactions between water molecules and the hydrophilic quaternary ammonium groups would lead to strong water adsorption around the quaternary ammonium groups. By contrast, the contact angle value of BTPPO membranes increases from 44.5 to 60.1°, attributed to the decreased hydrophilicity from BTPPO-1h to BTPPO-5h. Surprisingly, no obvious change in water uptake values is observed when the temperature increases from 25 to 65 °C for all BTPPO membranes. In general, the water uptake of ion exchange membrane increases with increasing the temperature because the swelling at elevated temperatures results in the increase in free space in the membrane matrix, facilitating water adsorption [44]. Such unusual phenomena demonstrate the positive effect of crosslinking on the swelling stability of BTPPO membranes.

3.5. Diffusion dialysis performance

Diffusion dialysis performance of BTPPO membranes is tested using HCl and FeCl$_2$ mixture solution as the typical model acidic waste solution. Fig. 6 shows the acid dialysis coefficient ($U_{H^+}$) and separation factor ($U_{H^+}/U_{Fe^{2+}}$) of different BTPPO membranes at 25 °C. From BTPPO-1h to BTPPO-5h membrane, $U_{H^+}$ values generally decrease from 0.062 to 0.041 m h$^{-1}$ while separation factor values gradually increase from 30.4 to 84.4. The former is due to the decrease in IEC determining the amount of the ion transport sites and the increased crosslinking degree hindering the ion transport while the latter is due to the enhanced crosslinking degree, making membrane much denser for ion sieving, where smaller protons permeate through membrane more quickly [14]. By contrast, our previous membrane prepared also from BPPO
ultrafiltration membrane but using polymer PEI as crosslinker showed $U_{H^+}$ of 0.063 m h$^{-1}$ and separation factor of 20.0 [36], respectively, BTPPO-1h membrane using small molecule BTDA as crosslinker shows approximate 50% increase in separation factor under the same $U_{H^+}$, attributing to the weaker steric hindrance consequently the more sufficient crosslinking of the membrane. Further compared with our previous membrane based on BPPO ultrafiltration membrane but using $N,N,N',N'$-tetramethylethylenediamine (TEMED) as simultaneous crosslinker and quaternization agent, whose highest $U_{H^+}$ value is only 0.043 mol h$^{-1}$ [37], that is, BTPPO-1h membrane herein shows approximate 50% increase in $U_{H^+}$. The results suggest the significant improvement in diffusion dialysis when utilizing the functionalization agent herein.

For comparison, the data on $U_{H^+}$ versus separation factor of typical anion exchange membranes recently reported in the literature for the acid recovery from HCl/FeCl$_2$ solution are included in Fig. 7 (and Table 3). The upper bound line is drawn to show the highest $U_{H^+}$ at a given separation factor in an anion exchange membrane so far. BTPPO membranes show highest $U_{H^+}$ at a given separation factor. This is a clear indication that high $U_{H^+}$ may be achieved with good separation property herein. The results suggest that BTPPO membranes are superior as compared to current dense membranes. Specifically, the commercial DF-120 membrane with a thickness of 320 micrometers exhibits a $U_{H^+}$ value of 0.0085 m h$^{-1}$ and separation factor value of 20. In other words, our membranes show 4.1-6.3 times higher in proton permeability and 0.6-3.6 times higher in separation factor; the calculated acid recovery capacity can increase from 11.3 up to 82.4 L m$^{-2}$ d$^{-1}$, with a 64% increasing acid purity from DF-120 to our membrane.

We postulated that the difference in ion transport mechanism in the membrane caused by the special membrane microstructure is the main reason why BTPPO ultrafiltration membranes show quite higher acid dialysis coefficient as compared with the dense membrane. Typically, the transport of small molecules (e.g. ions) across a dense or nanoporous polymer membrane
follows a solution-diffusion mechanism involving sorption of solutes into the membrane, diffusion across the membrane and desorption of solutes out of the membrane [45, 46]. Among these process, diffusion across the membrane under hopping mechanism or vehicular mechanism is the most important and largely depending on the free volume of the polymer [45-47]. Fig. 8 shows the possible ion transfer mechanisms in a dense or hierarchical porous ultrafiltration membranes. For dense membrane, ion transfer rate is low because of the less free volume and the high thickness. For hierarchical porous ultrafiltration membrane, ions may firstly transport through the thin skin layer (0.85 micrometer) via nano-channels rather than the wall matrix because of the larger free volume. The transport rate should be higher than dense membrane with the same thickness also because of the larger free volume. Afterwards, ion transport rate in the supporting layer should be accelerated because of the abundant water absorbed in the finger-like macro-channels [45, 46]. Obviously, the ion diffusivity across the whole ultrafiltration membrane is quite higher than that across the dense membrane.

3.6. Thermal stability

The thermal stabilities of BPPO and the fabricated BTPPO ultrafiltration membrane were studied by TGA. Their typical TGA curves are shown in Fig. 9. For BPPO membrane, its starting degradation temperature is about 250 °C. For BTPPO membrane, the decrease in weight before 100 °C is attributed to the loss of the absorbed water because of strong hydrophilicity of the quaternary ammonium group that attracting water from the atmosphere. This behavior has been commonly found in other polymeric ion exchange membranes and should be ignored. Therefore, BTPPO-4h shows starting decomposition temperature about 150 °C related to the degradation of quaternary ammonium groups [48]. These results suggest the good thermal stability of BTPPO membranes and can fully satisfy the need of diffusion dialysis application.

3.7. Chemical stability
Good chemical stabilities in acid environment are required for anion exchange membranes used in diffusion dialysis. To investigate the chemical stability of the membranes in acid environment, the selected BTPPO-4h membrane was immersed in HCl/FeCl\textsubscript{2} feed solution at 25 and 65 °C for 7 d. Fig. 10 shows the changes of the weight of the selected BTPPO-4h membrane over different immersion times. In addition to the excellent thermal stability, BTPPO membrane had good chemical stability. BTPPO-4h membrane maintained its weight even after immersion in HCl/FeCl\textsubscript{2} at 65 °C for 7 d. The diffusion dialysis performance of the BTPPO-4h membrane after immersed in HCl/FeCl\textsubscript{2} solution at 65 °C was tested. The membrane showed a \( U_{H^+} \) of 0.045 m h\textsuperscript{-1} and a separation factor of 72.5, both of which are similar to the corresponding values of the membranes before the treatment (0.044 m h\textsuperscript{-1} and 73.6, respectively).

**Conclusion**

A facile approach to prepare crosslinked and quaternized anion exchange membranes with asymmetrically porous micro-structure was developed. BPPO ultrafiltration membrane prepared through the phase inversion method was firstly in situ crosslinked by BTDA and then quaternized by TMA. The resulting membranes were evaluated in terms of ion exchange capacity, water uptake and diffusion dialysis performance. Our study showed that the anion exchange membranes had excellent swelling, thermal and chemical stabilities and high proton permeability and separation factor, due to the unique micro-structure of the BPPO ultrafiltration membrane (small effective thickness of the selective layer (~0.85 µm) and high porosity of the supporting layer). In particular, BTPPO membranes showed proton dialysis coefficients of 0.041-0.062 m h\textsuperscript{-1} and separation factors of 30.4-82.4. The diffusion dialysis performance of BTPPO membranes is superior to those membranes reported in the literature, 4.1-6.3 times greater in proton permeability and 0.6-3.6 times higher in separation factor than the commercial DF-120 membrane at the same test condition. Furthermore, BTPPO
membranes show a significant improvement in diffusion dialysis performance compared with our previous work, in which BPPO ultrafiltration membrane was also used but crosslinked and quaternized by different agents. These results demonstrate that BTPPO membranes have great potential for practical diffusion dialysis applications, thereby significantly improving acid recovery efficiency.

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References


[38] T. Xu, D. Wu, L. Wu, Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-A versatile starting polymer for proton conductive membranes (PCMs), Progress in Polymer Science (Oxford), 33 (2008) 894-915.


Captions of figures and tables

Scheme 1. Schematic diagram of the preparation of crosslinked and quaternized BTPPO ultrafiltration membrane.

Fig. 1. (a) Survey spectra and (b) high resolution N1s spectra of BPPO, BBPPO-4h and BTPPO-4h membranes.

Fig. 2. The top surface, bottom surface, cross section and active layer SEM images of BPPO, BBPPO-2h, BBPPO-4h and BBPPO-5h membranes.

Fig. 3. SEM images of BTPPO-2h and BTPPO-4h membranes.

Fig. 4. Ion exchange capacity of BTPPO membranes.

Fig. 5. Water uptake and contact angle of BTPPO membranes.

Fig. 6. Diffusion dialysis performance of BTPPO membranes.

Fig. 7. Relation between acid dialysis coefficient and separation factor of BTPPO membranes.

The data on dense anion exchange membranes for diffusion dialysis from recent literatures are also included: DF-120 (Point 1), (Point 2) [14], (Point 3) [15], (Point 4) [16], (Point 5) [17], (Point 6) [18], (Point 7) [19], (Point 8) [20], (Point 9) [21], (Point 10)[22], (Point 11) [23] and (Point 12) [24].

Fig. 8. The ion transfer mechanism in a (a) dense anion exchange membrane or (b) an asymmetric porous BTPPO anion exchange membrane.

Fig. 9. TGA curves of BPPO and BTPPO-4h membrane.

Fig. 10. The weight percentage of the BTPPO-4h membranes after immersion in aqueous HCl/FeCl₂ solution at 25 and 65 °C for increasing lengths of time.

Table 1. Mechanical properties and acid dialysis coefficients (U_{H^+}) of membranes with different treatment procedure based on BPPO membranes.

Table 2. Atomic percentage calculated from XPS peak area for BPPO, BBPPO-4h and BTPPO-4h membranes.
Table 3. Ion exchange capacity (IEC), acid dialysis coefficient ($U_{H^+}$) and separation factor (S) of the reported membranes at 25 °C using HCl/FeCl$_2$ solution as model acidic waste solution.