

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

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26 **Abstract**

27 Diffusion dialysis for acid recovery from acidic waste solution suffers from the low process
28 capacity due to low proton permeability of current dense anion exchange membranes. In this
29 work, asymmetrically porous ultrafiltration membranes with a thin skin layer (e.g., <1
30 micrometer) were converted to diffusion dialysis membranes with a hierarchically porous
31 structure after *in situ* crosslinking and quaternization. Except for good thermal and chemical
32 stabilities, the resulting membranes exhibited an acid permeability coefficient as high as 0.041-
33 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
34 higher than the commercial DF-120 membrane, respectively. The acid recovery capacity can
35 be enhanced from 11.3 to 82.4 L m⁻² d⁻¹, with a 64% increase in acid purity when our new
36 membrane was used to replace the commercial DF-120 membrane. Moreover, these results are
37 also superior to most of the reported membranes. Therefore, the excellent performance and
38 simple preparation process endow our new diffusion dialysis membranes with great potential
39 for high-efficiency industrial acid recovery applications.

40 **Keywords:** diffusion dialysis, ultrathin, asymmetrically porous, acid recovery, acidic
41 wastewater

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51 **1. Introduction**

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

63 As the key component in diffusion dialysis, the anion exchange membrane should have high
64 acid permeability and salt rejection, and long-term stability including high chemical and
65 thermal stabilities to satisfy the demand of practical production. To date, most of the anion
66 exchange membranes used in diffusion dialysis are dense membranes. One type of them are
67 homogenous and symmetrical membranes, prepared by the direct evaporation of the polymer
68 solution to form the homogeneous membranes [13]. However, they are thick (several tens or
69 hundreds of microns) and dense in microstructure and show low ion permeability leading to
70 low process capacity and efficiency. For instance, a commercial dense membrane DF-120 with
71 a thickness of 320 micrometers has the proton (H^+) dialysis coefficient (U_{H^+}) of only 0.0085 m
72 h^{-1} at 25°C. Even various modifications have been conducted to improve the diffusion dialysis
73 performance of the symmetrically dense anion exchange membranes, the improvement remains
74 unsatisfying given its dense microstructure [14-24]. Another type of dense anion exchange
75 membranes for diffusion dialysis are asymmetric membranes, they can prepared from the

76 copolymerization of monomers within the pores of pre-formed porous membranes substrate
77 [25-28] or blending of the different polymer or additive components [29, 30]. Recently, the
78 method of electrospinning of quaternized polymer nanofibers, followed by solvent fumigation
79 and hot-press has been utilized to fabricate asymmetrically dense anion exchange membrane
80 [31]. Even though good diffusion dialysis performance can be achieved for asymmetric anion
81 exchange membrane, they are always complex in fabrication process and their large-scale
82 production is therefore limited

83 Ultrafiltration membranes are typical asymmetric and porous membranes simply prepared *via*
84 nonsolvent-induced phase inversion [32], and are widely used in water treatment [33-35].
85 Typically, they have a thin nanoporous skin layer with a thickness of sub-micrometer and a
86 thick and macroporous supporting layer. Considering the hierarchical porous structure of
87 ultrafiltration membrane, the high acid permeability of ultrafiltration membranes can be
88 expected after the modification to block the pores at the top surface and introduce the positively
89 charged groups into the membrane matrix. Since ultrafiltration membranes can be conveniently
90 prepared *via* the phase inversion technique [32], the conversion of ultrafiltration membranes is
91 a simple and effective method for the large-scale production of high-performance diffusion
92 dialysis membranes. In our previous work, we have demonstrated that asymmetrically porous
93 anion exchange membranes prepared from ultrafiltration membranes after crosslinking and
94 quaternization treatment show significantly high proton permeability for acid recovery by
95 diffusion dialysis [36, 37]. Specifically, anion exchange membranes prepared from
96 ultrafiltration membrane by the simultaneously crosslinking and quaternization with *N,N,N',N'*-
97 tetramethylethylenediamine (TEMED) showed highest acid permeability coefficient (U_{H^+}) of
98 0.043 m h^{-1} [37]. Moreover, anion exchange membranes prepared from ultrafiltration
99 membrane by crosslinking with polyethyleneimine (PEI) and subsequent quaternization with
100 trimethylamine (TMA) showed significantly increased U_{H^+} of 0.063 m h^{-1} , unfortunately, their

101 separation factor is quite lower because of the usage of the polymer crosslinker, which is
102 inadequate for fully crosslinking due to the high steric hindrance [36]. It is noted that the newly
103 reported work on the direct conversion of ultrafiltration membrane into diffusion dialysis
104 membrane is insufficient, it is still essential to optimize the functionalization process, such as
105 the investigation of the effect of the crosslinker type to obtain anion exchange membranes with
106 optimal diffusion dialysis performance.

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

122 **2. Materials and Methods**

123 **2.1. Materials**

124 Brominated poly(phenylene oxide) (BPPO, Mw~ 60,500) with a benzyl substitution ratio of
125 0.57 was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP), 1,

126 4-butanediamine (BTDA), trimethylamine (TMA), hydrochloric acid (HCl), anhydrous ferrous
127 chloride (FeCl_2), sodium carbonate (Na_2CO_3) and potassium permanganate (KMnO_4) were
128 purchased from Sigma-Aldrich, Australia, and used without further purification. Distilled
129 water was used throughout the experiments.

130 **2.2. Preparation of BPPO ultrafiltration membrane**

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

141 **2.3. Preparation of crosslinked and quaternized anion exchange membrane**

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

149 **2.4. Characterization**

150 **2.4.1. Scanning electron microscopy (SEM) analysis**

151 Scanning electron microscopy was undertaken with a Nova NanoSEM 450 FESEM, FEI,
152 USA.). The membrane samples were fixed on a SEM sample holder with double-sided carbon
153 tape and then sputter-coated with an around 0.5nm iridium layer. For the cross sectional
154 morphology observation, the membrane samples was firstly immersed in distilled water for 24
155 h, then the water on the membrane surface was removed using a piece of Kimtech tissue paper.
156 After that, the samples were fractured in liquid nitrogen to get clean cross sections.

157 **2.4.2. X-ray photoelectron spectroscopy (XPS) analysis**

158 X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD
159 spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K α source
160 at a power of 150 W (10 kV 15 mA), a hemispherical analyser operating in the fixed analyser
161 transmission mode and the standard aperture (analysis area: 0.3 mm \times 0.7 mm) The total
162 pressure in the main vacuum chamber during analysis was typically between 10⁻⁹ and 10⁻⁸
163 mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed
164 information about chemical structure, oxidation states etc., and high resolution spectra were
165 recorded from individual peaks at 40 eV pass energy (yielding a typical peak width for
166 polymers of 1.0) Each specimen was analysed at an emission angle of 0° as measured from the
167 surface normal. Assuming typical values for the electron attenuation length of relevant
168 photoelectrons the XPS analysis depth (from which 95 % of the detected signal originates)
169 ranges between 5 and 10 nm for a flat surface

170 **2.4.3. Thermogravimetric analysis (TGA)**

171 Thermal stability of the membrane sample was performed on a SII EXSTAR 6000 TG/DTA
172 6300 under argon flow and with a heating rate of 10 °C min⁻¹. Thermogravimetric analysis
173 (TGA) was carried out by TG/DTA 6300, SII EXSTAR 6000 at a heating rate of 10°C per
174 minute under pure argon.

175 **2.4.4. Water uptake**

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

$$182 \text{ Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \quad (1)$$

183 **2.4.5. Contact angle**

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

188 **2.4.5. Ion exchange capacity (IEC)**

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

197 **2.4.6. Chemical stability**

198 For investigation of the chemical stability of the prepared membranes in an acidic
199 environment, the membrane samples were immersed in an aqueous HCl (~1 mol/L)/FeCl₂ (~0.2
200 mol/L) mixture solution for different lengths of time at 25 and 65 °C, which is a harsh hot and

201 acidic environment for the membrane used in diffusion dialysis. The change in weight
202 percentage and diffusion dialysis performance by the acidic treatment was determined to
203 evaluate the membrane chemical stability.

204 **2.4.7. Diffusion dialysis tests**

205 Diffusion dialysis runs were performed in a cell with two chambers, which were separated by
206 a membrane with an effective area of 5.73 cm [14]. Prior to the test, the membranes were
207 conditioned for 1 day in the feed solution and washed thoroughly by water for 3-4 days until
208 pH neuter was achieved. Then the membrane was fixed between two chambers with top surface
209 facing feed solution. The feed side of the cell was filled with 140 ml of HCl (~1 mol/L)/FeCl₂
210 (~0.2 mol/L) mixture solution and the permeate side with 140 mL distilled water. During the
211 diffusion test, both compartments were stirred at identical rates to minimize concentration
212 polarization effects and the cell temperature was kept constant at 25 °C by a water bath.
213 Diffusion was allowed for 45 min and then the HCl/FeCl₂ solutions and water were removed
214 from both sides of the cell. The concentration of HCl in the solutions was determined by acid–
215 base titration with a standard Na₂CO₃ (0.05 mol L⁻¹) solution using methyl orange as indicator,
216 while the concentration of FeCl₂ was determined by the oxidation titration with purple KMnO₄
217 solution (0.001 mol L⁻¹) as simultaneous oxidizing agent and indicator.

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

$$221 \quad U = \frac{M}{At\Delta C} \quad (2)$$

222 where M is the amount of component transported in moles, A the effective area in m², t the
223 time in h, and ΔC the logarithm average concentration between the two chambers in moles m⁻³
224 and defined according to Eq. (3) as follows:

$$225 \quad \Delta C = \frac{(C_f^0 - C_d^t - C_f^t)}{\ln[(C_f^0 - C_d^t)/C_f^t]} \quad (3)$$

226 where C_f^0 and C_f^t are the feed concentrations at time 0 and t, respectively, and C_d^t the dialysate
227 concentration at time t. It should be noted that $(C_f^0 - C_d^t - C_f^t)$ is not equal to zero, because
228 water transport through the membrane will cause volume changes in the cell chambers during
229 the experiment [41].

230

231 **3. Results and Discussion**

232 **3.1. Chemical structure**

233

234 The membranes based on BPPO ultrafiltration membrane with different treatment procedures
235 were prepared and their proton dialysis coefficients (U_{H^+}) at 25 °C were tested. As shown in
236 Table 1, for BPPO ultrafiltration membrane treated with TMA (2#) only, it suffered from
237 serious swelling and its mechanical strength was too low for testing [36]. Moreover, the
238 pristine BPPO membrane (1#) and BBPPO ultrafiltration membrane only treated with BTDA
239 (3#) showed no proton permeability as there were no ion exchange groups in the membrane
240 matrix (See XPS spectra in Fig. 1). By contrast, BTPPO ultrafiltration membrane treated with
241 BTDA and TMA (4#) in turn showed proton dialysis coefficients of 0.062 m h^{-1} and separation
242 factor of 30.4. These results demonstrate the necessity of BTDA and TMA treatment for BPPO
243 ultrafiltration membrane modification for DD application.

244 The functionalization process as well as the chemical composition at the top surface were
245 determined using the XPS technique. Fig. 1 shows the survey spectra and high resolution
246 spectrum of the pristine BPPO, BBPPO-4h and BTPPO-4h membranes, respectively. The
247 peaks of O1s, N1s, C1s and Br3d are clearly presented in Fig. 1(a). From BPPO to BBPPO and
248 BTPPO, the intensity of N element increases while that of Br element decreases. As shown in
249 Table 2, from BPPO to BBPPO and BTPPO membranes, the atomic percentage of N and Br
250 element will increase from 4.48% to 5.08% and 7.54% and decrease from 4.69% to 2.48% and

251 2.20%, respectively, due to the conversion of $-\text{CH}_2\text{Br}$ groups to amine groups during the
252 functionalization process. The presence of newly formed quaternary ammonium group is
253 confirmed by the peak at 402.1 eV [42] in the high-resolution spectrum (Fig. 1(b)) for BTPPO
254 rather than BPPO and BBPPO membranes. That is the reason why BPPO and BBPPO
255 membranes showed no proton permeability in our preliminary work, attributing to the absence
256 of the anion exchange groups for ion transfer. These results confirm the successful
257 functionalization process and the introduction of quaternary ammonium groups as anion
258 exchange groups.

259 **3.2. Membrane morphology**

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

271 From BBPPO to BTPPO after further reacting with TMA, the pores at the top surface of
272 BTPPO membrane disappear due to the swelling effect of the hydrophilic quaternary
273 ammonium groups. Beyond that, no change can be observed for the morphology of BTPPO
274 membrane (Fig. 3) as compared with BBPPO membrane. These results suggest that the unique
275 micro-structure of the ultrafiltration membrane can be maximum remained for BTPPO

276 membranes except blocking the pores at their surfaces. Moreover, the thickness of the skin
277 layer as the effective thickness of BTPPO ultrafiltration membranes is about 0.85 μm . By
278 contrast, the conventional dense membrane always show dozens to hundreds μm in thickness,
279 the great decrease in low thickness and obviously porous structure can be expected to greatly
280 facilitate the proton permeability of the membrane.

281 **3.3. Ion exchange capacity**

282 It is well known that electrochemical properties of anion exchange membrane are
283 dependent on the amount of anion exchange groups that directly control ion transport in the
284 membrane matrix. In our work, BPPO ultrafiltration membranes were firstly crosslinked by
285 immersing in BTDA solution with different time along with the consumption of partial $-\text{CH}_2\text{Br}$
286 groups and then fully quaternized by TMA solution to convert the residual $-\text{CH}_2\text{Br}$ groups to
287 quaternary ammonium groups to obtain the final crosslinked and quaternized BTPPO
288 membranes. Distinctly, the above-mentioned first step determines not only the crosslinking
289 degree but also the density of quaternary ammonium groups of BTPPO membranes, which are
290 the key to the separation properties and proton permeability of the membrane for diffusion
291 dialysis, respectively.

292 The membrane properties including ion exchange capacity, water uptake, and diffusion
293 dialysis performance were investigated. From BTPPO-1h to BTPPO-4h membrane with the
294 increasing immersion time in BTDA, the ion exchange capacity (IEC) value, a measure of the
295 charge density, decreases from 1.45 to 1.01 mmol g^{-1} (Fig. 4), which was attributed to the
296 decrease in the amount of $-\text{CH}_2\text{Br}$ groups left for quaternization. From BTPPO-4h to BTPPO-
297 5h membrane with even a longer immersion time in BTDA solution, IEC value remained
298 unchanged. In other words, BPPO ultrafiltration membrane was already fully crosslinked after
299 immersed in BTDA solution for 4 h.

300 **3.4. Water uptake and contact angle**

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

316 **3.5. Diffusion dialysis performance**

317 Diffusion dialysis performance of BTPPO membranes is tested using HCl and FeCl₂ mixture
318 solution as the typical model acidic waste solution. Fig. 6 shows the acid dialysis coefficient
319 (U_{H^+}) and separation factor ($U_{H^+}/U_{Fe^{2+}}$) of different BTPPO membranes at 25 °C. From
320 BTPPO-1h to BTPPO-5h membrane, U_{H^+} values generally decrease from 0.062 to 0.041 m h⁻¹
321 while separation factor values gradually increase from 30.4 to 84.4. The former is due to the
322 decrease in IEC determining the amount of the ion transport sites and the increased crosslinking
323 degree hindering the ion transport while the latter is due to the enhanced crosslinking degree,
324 making membrane much denser for ion sieving, where smaller protons permeate through
325 membrane more quickly [14]. By contrast, our previous membrane prepared also from BPPO

326 ultrafiltration membrane but using polymer PEI as crosslinker showed U_{H^+} of 0.063 m h^{-1} and
327 separation factor of 20.0 [36], respectively, BTPPO-1h membrane using small molecule BTDA
328 as crosslinker shows approximate 50% increase in separation factor under the same U_{H^+} ,
329 attributing to the weaker steric hindrance consequently the more sufficient crosslinking of the
330 membrane. Further compared with our previous membrane based on BPPO ultrafiltration
331 membrane but using *N,N,N',N'*-tetramethylethylenediamine (TEMED) as simultaneous
332 crosslinker and quaternization agent, whose highest U_{H^+} value is only 0.043 mol h^{-1} [37], that
333 is, BTPPO-1h membrane herein shows approximate 50% increase in U_{H^+} . The results suggest
334 the significant improvement in diffusion dialysis when utilizing the functionalization agent
335 herein.

336 For comparison, the data on U_{H^+} versus separation factor of typical anion exchange
337 membranes recently reported in the literature for the acid recovery from HCl/FeCl₂ solution
338 are included in Fig. 7 (and Table 3). The upper bound line is drawn to show the highest U_{H^+} at
339 a given separation factor in an anion exchange membrane so far. BTPPO membranes show
340 highest U_{H^+} at a given separation factor. This is a clear indication that high U_{H^+} may be achieved
341 with good separation property herein. The results suggest that BTPPO membranes are superior
342 as compared to current dense membranes. Specifically, the commercial DF-120 membrane
343 with a thickness of 320 micrometers exhibits a U_{H^+} value of 0.0085 m h^{-1} and separation factor
344 value of 20. In other words, our membranes show 4.1-6.3 times higher in proton permeability
345 and 0.6-3.6 times higher in separation factor; the calculated acid recovery capacity can increase
346 from 11.3 up to $82.4 \text{ L m}^{-2} \text{ d}^{-1}$, with a 64% increasing acid purity from DF-120 to our membrane.

347 We postulated that the difference in ion transport mechanism in the membrane caused by the
348 special membrane microstructure is the main reason why BTPPO ultrafiltration membranes
349 show quite higher acid dialysis coefficient as compared with the dense membrane. Typically,
350 the transport of small molecules (e.g. ions) across a dense or nanoporous polymer membrane

351 follows a solution-diffusion mechanism involving sorption of solutes into the membrane,
352 diffusion across the membrane and desorption of solutes out of the membrane [45, 46]. Among
353 these process, diffusion across the membrane under hopping mechanism or vehicular
354 mechanism is the most important and largely depending on the free volume of the polymer [45-
355 47]. Fig. 8 shows the possible ion transfer mechanisms in a dense or hierarchical porous
356 ultrafiltration membranes. For dense membrane, ion transfer rate is low because of the less free
357 volume and the high thickness. For hierarchical porous ultrafiltration membrane, ions may
358 firstly transport through the thin skin layer (0.85 micrometer) *via* nano-channels rather than the
359 wall matrix because of the larger free volume. The transport rate should be higher than dense
360 membrane with the same thickness also because of the larger free volume. Afterwards, ion
361 transport rate in the supporting layer should be accelerated because of the abundant water
362 absorbed in the finger-like macro-channels [45, 46]. Obviously, the ion diffusivity across the
363 whole ultrafiltration membrane is quite higher than that across the dense membrane.

364 **3.6. Thermal stability**

365 The thermal stabilities of BPPO and the fabricated BTPPO ultrafiltration membrane were
366 studied by TGA. Their typical TGA curves are shown in Fig. 9. For BPPO membrane, its
367 starting degradation temperature is about 250 °C. For BTPPO membrane, the decrease in
368 weight before 100 °C is attributed to the loss of the absorbed water because of strong
369 hydrophilicity of the quaternary ammonium group that attracting water from the atmosphere.
370 This behavior has been commonly found in other polymeric ion exchange membranes and
371 should be ignored. Therefore, BTPPO-4h shows starting decomposition temperature about 150
372 °C related to the degradation of quaternary ammonium groups [48]. These results suggest the
373 good thermal stability of BTPPO membranes and can fully satisfy the need of diffusion dialysis
374 application.

375 **3.7. Chemical stability**

376 Good chemical stabilities in acid environment are required for anion exchange membranes used
377 in diffusion dialysis. To investigate the chemical stability of the membranes in acid
378 environment, the selected BTPPO-4 h membrane was immersed in HCl/FeCl₂ feed solution at
379 25 and 65 °C for 7 d. Fig. 10 shows the changes of the weight of the selected BTPPO-4h
380 membrane over different immersion times. In addition to the excellent thermal stability,
381 BTPPO membrane had good chemical stability. BTPPO-4h membrane maintained its weight
382 even after immersion in HCl/FeCl₂ at 65 °C for 7 d. The diffusion dialysis performance of the
383 BTPPO-4 h membrane after immersed in HCl/FeCl₂ solution at 65 °C was tested. The
384 membrane showed a U_{H^+} of 0.045 m h⁻¹ and a separation factor of 72.5, both of which are
385 similar to the corresponding values of the membranes before the treatment (0.044 m h⁻¹ and
386 73.6, respectively).

387 **Conclusion**

388 A facile approach to prepare crosslinked and quaternized anion exchange membranes with
389 asymmetrically porous micro-structure was developed. BPPO ultrafiltration membrane
390 prepared through the phase inversion method was firstly in situ crosslinked by BTDA and then
391 quaternized by TMA. The resulting membranes were evaluated in terms of ion exchange
392 capacity, water uptake and diffusion dialysis performance. Our study showed that the anion
393 exchange membranes had excellent swelling, thermal and chemical stabilities and high proton
394 permeability and separation factor, due to the unique micro-structure of the BPPO
395 ultrafiltration membrane (small effective thickness of the selective layer (~0.85 μm) and high
396 porosity of the supporting layer). In particular, BTPPO membranes showed proton dialysis
397 coefficients of 0.041-0.062 m h⁻¹ and separation factors of 30.4-82.4. The diffusion dialysis
398 performance of BTPPO membranes is superior to those membranes reported in the literature,
399 4.1-6.3 times greater in proton permeability and 0.6-3.6 times higher in separation factor than
400 the commercial DF-120 membrane at the same test condition. Furthermore, BTPPO

401 membranes show a significant improvement in diffusion dialysis performance compared with
402 our previous work, in which BPPO ultrafiltration membrane was also used but crosslinked and
403 quaternized by different agents. These results demonstrate that BTPPO membranes have great
404 potential for practical diffusion dialysis applications, thereby significantly improving acid
405 recovery efficiency.

406

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411 **References**

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547 **Captions of figures and tables**

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

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

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

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

555 **Fig. 4.** Ion exchange capacity of BTPPO membranes

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

557 **Fig. 6.** Diffusion dialysis performance of BTPPO membranes.

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

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

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

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

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

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

570 **Table 2.** Atomic percentage calculated from XPS peak area for BPPO, BBPPO-4h and
571 BTPPO-4h membranes

572 **Table 3.** Ion exchange capacity (IEC), acid dialysis coefficient (U_{H^+}) and separation factor (S)
573 of the reported membranes at 25 °C using HCl/FeCl₂ solution as model acidic waste solution.