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## Porous diffusion dialysis membranes for rapid acid recovery

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## ABSTRACT

To enhance the proton permeability of the anion exchange membranes used in diffusion dialysis, porous ultrafiltration membrane with a thin skin layer rather than the dense membrane was utilized for the preparation of diffusion dialysis membrane. In particular, brominated poly (phenylene oxide) (BPPO) ultrafiltration membrane was fabricated *via* a phase inversion method and then modified by crosslinking with polyethyleneimine (PEI) and subsequent quaternization with trimethylamine (TMA) *via* nucleophilic substitution reaction. Diffusion dialysis related properties of the membranes such as water uptake, ion exchange capacity, and thermal and swelling stabilities were investigated. Due to the special structure of the membranes (i.e., high porosity and low thickness of the top layer (sub-1 μm), as confirmed by scanning electron microscopy) the optimal membrane exhibited 6.4 times higher acid dialysis coefficient for HCl recovery from HCl/FeCl<sub>2</sub> solution than the commercial DF-120 (thickness=320 μm) membrane at the similar separation factor. The calculated acid recovery capacity can increase from 11.3 up to 83.7 L m<sup>-2</sup> d<sup>-1</sup> by replacing DF-120 with our optimal membrane. Our findings show the porous membranes developed here have great potential for high-efficiency acid recovery through diffusion dialysis process.

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## 1. Introduction

Huge amounts of acidic waste solutions are produced from industrial production processes [1–4], direct disposal of these solutions not only pollutes the environment but also causes the loss of economic benefits. Diffusion dialysis as an attractive separation technology has been widely applied to recover inorganic or organic acid from waste solutions due to the unique advantages of diffusion dialysis especially the environmental benignity and low energy consumption [5–8]. Diffusion dialysis separation process utilizing anion exchange membrane (AEM) is driven by concentration gradient, in which the solutes spontaneously pass through AEM from high to low concentration side [9]. Therefore the external power is only required for the solution circulation. As the core component for diffusion dialysis, AEMs play the central role in the process. In addition to long-term stability including high acidic resistance and thermal stability, they are required to possess high acid dialysis coefficient for large-scale practical application of acid recovery [10,11].

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Currently, most of AEMs used in diffusion dialysis for acid recovery are dense membranes. They are commonly prepared by the direct evaporation of the solution of polymer (homogeneous membrane) such as polysulfone, polystyrene, and poly(phenylene oxide) [12], or by the copolymerization of monomers within the pores of pre-formed porous membranes substrate (heterogeneous membrane) [13–16]. However, they are always compact in microstructure and thick (several tens or hundreds of microns), which can hinder ion transport in the membrane [12]. For example, the commercial DF-120 membrane with a thickness of 320 μm has proton dialysis coefficient ( $U_{H^+}$ ) of only 0.0085 m h<sup>-1</sup> at 25 °C and its processing capability for acid recovery from this acidic waste solution is only about 11.3 L m<sup>-2</sup> d<sup>-1</sup>. To date, the various methods have been employed for the modification of dense AEMs [17–24], however, valuable improvement in proton permeability is still difficult.

To this end, we anticipate that an asymmetrical membrane with porous structure should possess higher proton permeability, which can be further enhanced if the thickness can be reduced. Ultrafiltration membranes are porous and asymmetrical membrane prepared *via* a phase inversion method, and they have a very thin and nanoporous skin layer, and a thick and macroporous supporting layer [25]. Considering the porosity and low thickness

of skin layer (sub-1  $\mu\text{m}$ ), there is a great potential for ultrafiltration membrane to be used in diffusion dialysis application after modifications such as crosslinking treatment. Recently, Wu et al. prepared a series of membranes by immersing ultrafiltration membranes in multisilicon copolymer solution, followed by sol-gel reaction to get the membrane for diffusion dialysis application [26]. However, these membranes showed low  $U_{\text{H}^+}$  of only 0.020–0.025  $\text{m h}^{-1}$  at 25  $^{\circ}\text{C}$ . The results should be due to the direct immersion of multisilicon copolymer, which formed an inorganic –Si–O–Si layer completely blocking all the pores of the resultant membranes. Therefore, the advantages of the asymmetric porous structure of ultrafiltration membrane were not taken.

In the present paper, ultrafiltration membrane was crosslinked by treatment of water soluble polyethyleneimine (PEI) solution. Specifically, brominated poly(phenylene oxide) (BPPO) with good stability and strength, and easiness for quaternization was chosen as starting material for ultrafiltration membrane preparation [27], and it was crosslinked by PEI. The original thickness and asymmetrically porous structure of the pristine ultrafiltration membrane was maintained and thus high proton permeability with good separation properties of the resultant AEMs could be expected. The modification process and the effects of the microstructure of ultrafiltration membrane on the membrane properties and performance will be also investigated.

## 2. Experimental

### 2.1. Materials

Brominated poly(phenylene oxide) (BPPO,  $M_w \sim 60,500$ ) with a benzyl substitution ratio of 0.57 was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP, 99.5%), poly(ethyleneimine) solution (PEI, 50 wt%,  $M_w \sim 750,000$ ), trimethylamine (TMA), hydrochloric acid (HCl), anhydrous ferrous chloride ( $\text{FeCl}_2$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and potassium permanganate ( $\text{KMnO}_4$ ) were purchased from Sigma-Aldrich, Australia, and used without further purification. Distilled water was used throughout.

### 2.2. Preparation of BPPO ultrafiltration membrane

BPPO polymer was used as the main component for membrane casting. It was firstly dissolved in NMP to form BPPO/NMP polymer casting solution with different concentrations (polymer content = 25, 30, 35 wt%). After ultrasonication, the resultant solution was left to stand overnight until no bubbles were observed. The membranes were prepared by using a Gardco<sup>®</sup> adjustable micrometer film applicator with a stainless steel blade (Paul N. Gardner Company, Inc. USA). About 5 mL of the polymer solution was cast on a clean glass plate with a gap of 200, 250 or 300  $\mu\text{m}$ . Afterwards the membrane was solidified in a coagulation bath of distilled water for several minutes. The resulting membranes were washed thoroughly and soaked in the distilled water overnight before use.

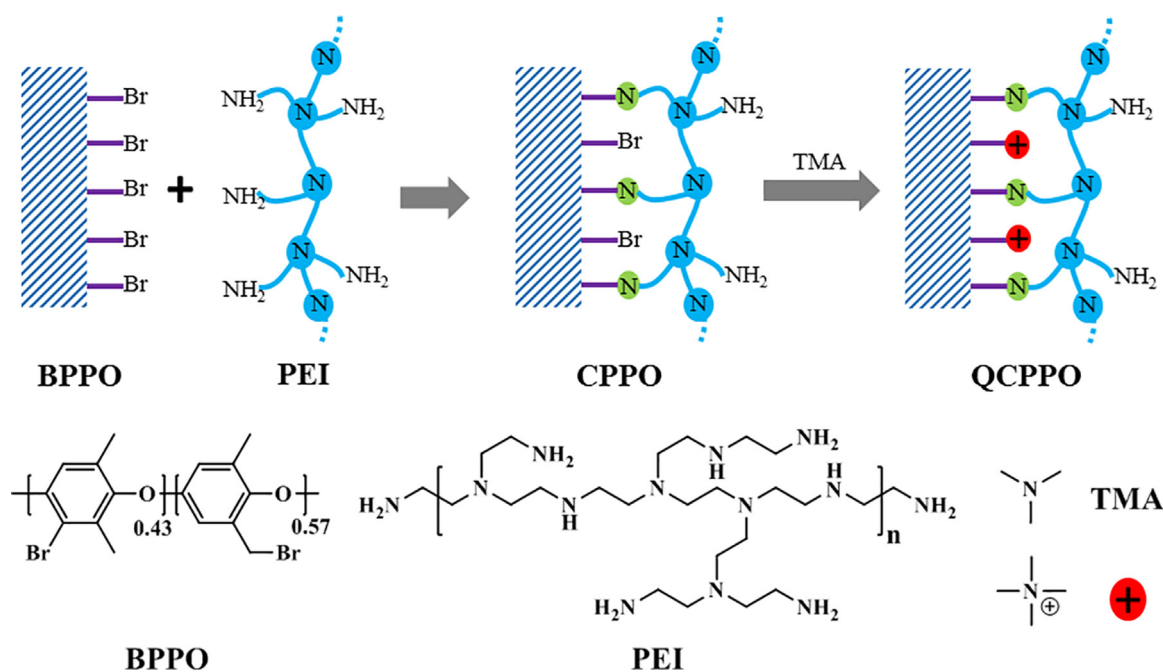
### 2.3. Preparation of crosslinked and quaternized anion exchange membrane

As shown in Scheme 1, the obtained BPPO ultrafiltration membranes prepared from different concentrations and thicknesses of the casting solution were firstly immersed in an aqueous PEI solution (10 wt%) at 40  $^{\circ}\text{C}$  for 24 h to ensure the full crosslinking of BPPO ultrafiltration membranes, which were designated as CPPO membranes. After washing thoroughly with water, the membranes were then immersed in an aqueous TMA solution (1 mol  $\text{L}^{-1}$ ) at 30  $^{\circ}\text{C}$  within given times. The final quaternized and crosslinked BPPO porous AEMs were designated as QCPPA membranes.

### 2.4. Membrane characterization

#### 2.4.1. SEM analysis

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 0.5 nm iridium layer. For the cross-sectional morphology observation, the membrane samples were



Scheme 1. Schematic diagram of the preparation of the crosslinked and quaternized QCPPA AEMs.

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