



Preparation of porous diffusion dialysis membranes by functionalization of polysulfone for acid recovery



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ABSTRACT

Asymmetrically porous anion exchange membranes for acid recovery by diffusion dialysis are prepared by one-step functionalization of chloromethylated polysulfone (PSF) ultrafiltration membrane *via* reaction with N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA) to achieve simultaneous crosslinking and quaternization. The performance of the resulting TMPDA modified PSF (TPSF) membranes can be easily tailored by controlling the reaction time in TMPDA solution and thus the charged density and crosslinking degree. The TPSF membranes exhibit excellent diffusion dialysis performance, especially high acid dialysis coefficient, stemming from the porous matrix and thin selective layer ($< 0.6 \mu\text{m}$). The optimized TPSF membrane has an acid dialysis coefficient of 0.065 m h^{-1} and a separation factor of 34.0, which are 6.6 and 0.84 times greater than the corresponding values of the commercial DF-120 membranes at the same testing condition using a mixture of HCl and FeCl_2 solution as feed solution. The membranes reported in this work are promising for scale-up for industrial acid recovery applications.

1. Introduction

Anion exchange membrane (AEM) is a positively charged membrane for anion conduction. AEMs have so far attracted growing attention for many applications such as in alkaline fuel cells (AFCs) [1–3], all vanadium flow battery (VRB) [4–6] and electro dialysis (ED) [7–9]. In addition, diffusion dialysis employing an AEM is a promising process for the treatment of acidic wastewater produced in industrial processes [10–14], because of its significant advantages over many other common methods for acid recovery in terms of low cost and environmental friendliness [15–17]. AEM is the core component in determining the process efficiency of diffusion dialysis and the purity of the recovered acid. It is noted that diffusion dialysis is a spontaneous process without external power and its driving force comes from the concentration gradient of the two solutions separated by AEM [16]. Moreover, the cost of acidic wastewater treatment has increased in recent years [18]. So the development of an AEM with high acid permeability to enhance the diffusion dialysis process capacity is of great interest.

The dense AEMs, including the homogeneous [16] and pore-filled

AEMs [19–22], have been the main focus for many years. Although many strategies had been developed to modify dense AEMs for diffusion dialysis, their performance remained unsatisfied given their dense morphology and large thickness [23–33]. Obviously, the thickness of AEMs should be reduced to improve acid dialysis coefficient [22,34]. However, the decrease in the dense membrane thickness results in reduced mechanical strength and acid-salt selectivity [34].

Until recently, ultrafiltration membranes have been considered as the membrane matrix to design mechanically robust AEMs with asymmetric microstructure composing of a thin ($\sim 1 \mu\text{m}$) nanoporous selective layer and a thick (50–150 μm) macroporous supporting layer [35]. The large-pore supporting layer provides sufficient mechanical strength but presents minimal ion transport resistance [36]. Very recently, our group demonstrated that it is an effective way to use porous ultrafiltration membrane as substrate to prepare high-performance AEMs for diffusion dialysis [37–39]. Specifically, brominated poly(phenylene oxide) (BPPO) polymer was used as the starting material to produce ultrafiltration membrane, which was then cross-linked and quaternized to obtain the porous AEMs, *via* the nucleophilic substitution between reactive $-\text{CH}_2\text{Br}$ groups and amine agents. The

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ion transport rate through the membrane was tremendously enhanced because the asymmetrically porous structure with a thin selective layer resulted in low ion permeation resistance; hence, simultaneous enhancements in both high acid permeability and high acid-salt selectivity were realized.

It is noted that only BPPO was investigated as the starting material for the membrane fabrication using direct conversion of ultrafiltration membrane. Therefore, it should be interesting to use other polymers to prove the applicability of this strategy, and it is also valuable to further investigate the polymer type to optimize the resulting membrane performance for diffusion dialysis application. Note that diffusion dialysis process has been widely used in many countries [16], but research is still needed to improve the process efficiency and operating cost. As the core component, the AEM mainly is the main contributor to the cost of the diffusion dialyzer. Therefore, the reduction of the cost of membrane fabrication is important for the development of low-cost diffusion dialysis process. BPPO is a less favored polymer for ultrafiltration membrane fabrication, and its price is high because of the limited large-scale production. By contrast, polysulfone (PSF) is a commercial polymer with a much lower price, and it has been widely used for the fabrication of ultrafiltration membranes [40–42]. The chloromethylation of PSF is very mature and of low cost for production of chloromethylated PSF (CMPSF) [43,44]. Until now, PSF polymer has not been used for the fabrication of the porous AEMs. Therefore, the scientific and economic values can be expected when BPPO is replaced with PSF as the starting material for the membrane preparation. In our previous work, we found that PSF ultrafiltration membrane [45] had smaller pore size at the top surface than BPPO ultrafiltration membrane [46] at the same condition. This indicates that the higher acid-salt selectivity of the resultant AEMs can be achieved when BPPO is replaced with PSF for the fabrication of porous AEMs.

In the present work, chloromethylated PSF ultrafiltration membranes were prepared by simple non-solvent phase immersion, followed by one-step functionalization of simultaneous crosslinking and quaternization by immersing the membranes in the aqueous solution of the bifunctional agent of *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA). The membrane structure and morphology as well as diffusion dialysis related performance were investigated in detail, and finally the comparison between our new membranes and other reported membranes was made.

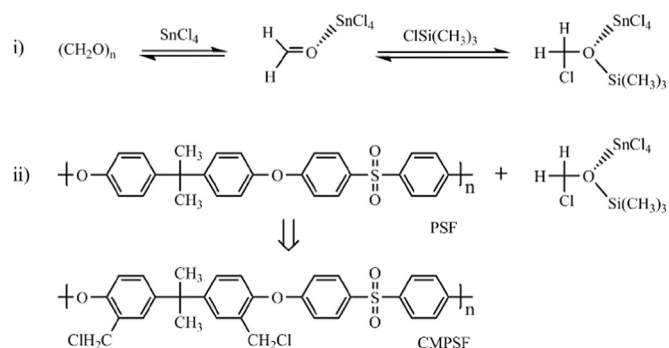
2. Experimental

2.1. Materials

Polysulfone (PSF, $M_w \sim 35,000$), anhydrous ferrous chloride (FeCl_2 , 98%), chloroform ($\geq 99\%$), paraformaldehyde (95%), trimethylchlorosilane ($\geq 97\%$), stannic chloride (SnCl_4 , 99%), 1-methyl-2-pyrrolidone (NMP, 99.5%) and *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA, $\geq 99\%$) were purchased from Sigma-Aldrich (Australia). Hydrochloric acid was purchased from Ajax Finechem Pty Ltd, Australia. Deionized water was used throughout the experiments.

2.2. Synthesis of CMPSF polymer

As shown in Scheme 1, chloromethylated polysulfone (CMPSF) was fabricated according to the reported method [47]: 10 g of PSF was added into 500 mL of chloroform in a flask equipped with a reflux condenser to form a homogenous solution under stirring, 6.78 g of paraformaldehyde and 24.6 g of trimethylchlorosilane were added into the PSF solution; afterwards, 1.178 g stannic chloride was added dropwise, the resulting solution was heated at 50 °C for 48 h. The final CMPSF was obtained by pouring the solution into ethanol bath, followed by drying at 60 °C in an oven for 12 h.



Scheme 1. Schematic illustration of CMPSF synthesis process.

2.3. Preparation of CMPSF ultrafiltration membrane

CMPSF ultrafiltration membrane was prepared *via* the non-solvent phase inversion method [46]. A 25 wt% CMPSF/NMP solution was firstly formed by dissolving CMPSF polymer in NMP. After ultrasonication to remove the bubbles, the CMPSF/NMP solution was cast onto a glass plate using a Gardco® adjustable micrometer film applicator with a stainless steel blade (Paul N. Gardner Company, Inc. USA), whose gap was set as 250 μm . After immersing the glass plate into a water bath for non-solvent phase inversion, the CMPSF ultrafiltration membrane was obtained.

2.4. Preparation of porous TPSF AEMs

As shown in Scheme 2, porous AEMs were prepared similar to our previous work [39]. The pre-formed CMPSF ultrafiltration membrane was simply immersed in 1 mol L^{-1} TMPDA solution at 60 °C for different times to tailor the membrane microstructure and diffusion dialysis related performance. The final AEMs prepared from CMPSF ultrafiltration membrane treated by TMPDA were named TPSF-X h AEMs, where X h is the immersion time of CMPSF ultrafiltration membrane in TMPDA solution.

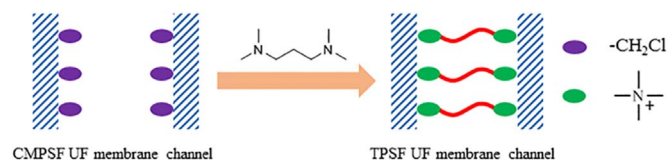
2.5. Membrane characterization

2.5.1. NMR, XPS, SEM and TGA

The degree of chloromethylation (DC) of CMPSF was determined using a Bruker Avance 400 (9.4 T magnet) nuclear magnetic resonance (NMR) spectrometer operating at 400 MHz. X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K α source operating at a power of 150 W (10 kV, 15 mA). The membrane morphologies were investigated using a scanning electron microscope (FEI Magellan Nano SEM 450 FEG SEM, USA). Thermogravimetric analysis (TGA) was conducted for thermal stability investigation using a TG-DTA/DSC, NETZSCH 449 F3 thermal gravity analyzer. The TGA measurement was performed by heating the sample from 30 to 800 °C in flowing argon at a heating rate of 10 °C min^{-1} .

2.5.2. Ion exchange capacity (IEC)

The membrane sample was firstly immersed in 0.2 mol L^{-1} NaOH aqueous solution at 25 °C for 12 h to ensure that all Cl^- ions within the membrane were ion-exchanged with OH^- . After thoroughly washing



Scheme 2. Schematic of the fabrication of porous TPSF AEMs.

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