



A polysulfone-based anion exchange membrane for phosphoric acid concentration and purification by electro-electrodialysis



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ABSTRACT

A series of quaternary ammonium polysulfone (QAPSU) anion exchange membranes used the chlorotrimethylsilane instead of toxic chloromethyl methyl ether and quaternized-functionalized by trimethylamine ethanol solution were prepared. The effect of chloromethylation reaction time on membrane morphologies and physiochemical properties such as ion exchange capacity, water swelling, and membrane area resistance, mechanical and thermal stabilities was investigated. When being applied in electro-electrodialysis (EED) for purifying phosphoric acid solution, the QAPSU membranes exhibit high purification efficiency, especially all the metal ions (Fe, Mg, Ca) removal rates reach over 60%, which suggests that the QAPSU membranes have a high potential for EED application.

1. Introduction

As the second most produced acid in the world, phosphoric acid is mainly obtained by the wet process [1]. However, the wet phosphoric acid contains a large number of impurities (Fe, Mg, Ca) [2]. Therefore, the purification of wet phosphoric acid is a major challenge, and a variety of methods, such as solvent extraction [3,4], precipitation [5,6] and adsorption on activated carbon [7], have been used to eliminate metallic impurities. However, these methods have many disadvantages such as long treatment time, complex experimental procedure, and high cost. Therefore, it is interesting to develop new technology for purifying phosphoric acid.

Membrane technologies containing reverse osmosis, nanofiltration [1] and electrodeionization process [2] etc., can be used to purify wet phosphoric acid solution. Electro-electrodialysis (EED) is a type of membrane separation technology with a single ion exchange membrane (IEM) driven by electrical potential gradient, which is easy to use without chemicals consumption (low cost) and waste generation (environmental friendliness) [8]. The EED technique therefore has been extensively applied in separating, preparing and concentrating acids [9–12], bases [13–15] and salts [16]. Theoretical calculation and experimental analysis have proved that it is feasible to use EED technique to purify wet phosphoric acid [17,18]. A high phosphoric acid yield and low metallic impurity content can also be achieved by this technique [19,20].

As the most important component of EED device, the IEM is required to have high ion transport efficiency, good mechanical and dimension stabilities [21]. To date, for commercially IEMs, the cation exchange membranes (CEMs) can be prepared in a reliable way in the industry, whereas the preparation of anion exchange membranes (AEMs) still present some technical problems in chloromethylation and quaternization process [22]. Chloromethyl methyl ether, the most frequently used chloromethylation reagent, is a well-known poison and cancerogen [23,24]. On the other hand, immersing chloromethylation membranes in trimethylamine (TMA) aqueous solution is required to obtain the quaternary ammonium AEM. However, it is usually accompanied by crack formation on the AEMs surface. Moreover, it is difficult to control the quaternization degree of the final materials due to low heterogeneous quaternization efficiency [25]. Hence, it is very important to choose a non-toxic chloromethylation reagent for AEM preparation with improved efficiency in quaternary ammonium reaction.

Polysulfone (PSU), with low price, excellent thermal and mechanical properties, has been widely used for the AEM fabrication in fuel cell [26], all-vanadium flow battery [27] and ionic polymer metal composite actuator field [28]. These advantages make PSU as the starting material for AEM preparation with the scientific and economic values. In this work, PSU-based AEMs was prepared by a simple, non-toxic chlorotrimethylsilane instead of chloromethyl methyl ether, followed by adding TMA ethanol solution to produce quaternary ammonium polysulfone (QAPSU). The QAPSU AEM was obtained through drop-

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casting and solvent evaporation. Their related structures, morphologies, and performances were investigated via controlling chloromethylation reaction time. The phosphoric acid solution purified efficiency of the obtained QAPSU membranes was also studied and compared with that of a commercial membrane LE 1201.

2. Experimental section

2.1. Materials

Polysulfone (PSU, $M_w = 57,500$) was obtained from BASF SE and dried 24 h under vacuum at 45 °C before use. Chloroform (CHCl_3), dimethylsulfoxide (DMSO), N, N-dimethylformamide (DMF), N-Methyl pyrrolidone (NMP) and trimethylamine (TMA) ethanol solution were purchased from Shanghai Sinopham Chemical Reagent Co. Ltd. (China). Chlorotrimethylsilane [$(\text{CH}_3)_3\text{SiCl}$], tin chloride anhydrous, paraformaldehyde were provided by Aladdin Industrial Co. Ltd. (China). Commercial membrane LE 1201 [Thickness = 240 μm , ion exchange capacity (IEC) = 1.90 mmol/g, water uptake (WU) = 31.0%, membrane area resistance (R_m) = 2.4 $\Omega \text{ cm}^2$] was purchased from Hangzhou Grion Environmental Technology Co. Ltd. (China). Simulated wet phosphoric acid solution containing 5.0 wt% H_3PO_4 , 0.11 wt% Fe, 0.07 wt% Mg, and 0.04 wt% Ca was used by self-made. Doubly distilled deionized water was used throughout this study.

2.2. Polymer synthesis and membrane preparation

The dried PSU (15 g) was completely dissolved in CHCl_3 (300 mL) with a mechanical stirrer at 30 °C. After adding paraformaldehyde (10.1 g) into the PSU solution, chlorotrimethylsilane (42.5 mL) and tin chloride anhydrous (0.4 mL) were added dropwise, respectively. The obtained mixture solution was stirred at 50 °C for 10, 20, 30, 40 and 60 h, respectively. The crude product was obtained by precipitating the mixture solution in methanol and washing the precipitate with methanol and deionized water for several times. After the crude product was dried in a vacuum oven at 45 °C for 24 h, the chloromethylated polysulfone (CMPSU) was obtained.

The dried CMPSU was dissolved in DMF to form a homogeneous solution of 10 wt% at 40 °C. Subsequently, TMA ethanol solution (molar ratio of TMA to CH_2Cl is about 3) was added into the CMPSU solution and stirred for 24 h to produce quaternary ammonium polysulfone (QAPSU). The resulting QAPSU solution was cast onto a clean flat glass plate. The solvent was removed by evaporation in an oven at 60 °C for 12 h, and the residual solvent was further removed at 80 °C under vacuum to obtain the transparent and flexible membrane. Finally, the membrane was immersed in 0.5 mol/L NaCl solution at room temperature for 24 h to ensure the membrane as Cl⁻ form. The obtained membrane was washed adequately and kept in deionized water to remove residual ions before use. The thickness of dried QAPSU membranes was measured in the range of 50–70 μm with a digital micrometer.

2.3. Membrane characterization

2.3.1. Structure and morphology

The functional groups of the polymers were measured in the range of 4000–650 cm^{-1} by ATR-FTIR spectrometer (Equinox 55, Bruker). Thermal stability of polymers was analyzed from 30 °C to 700 °C at the rate of 10 °C/min under nitrogen atmosphere with a TGA-7 analyzer (Perkin-Elmer). ^1H NMR spectra were recorded on a Bruker AV400 NMR spectrometer at 300 MHz and with tetramethylsilane (TMS) as internal reference. The degree of chloromethylation (DCM) of CMPSU can be determined via ^1H NMR:

$$\text{DCM} = \frac{3 \cdot \text{Area}_{\text{CH}_2\text{Cl}}(\delta)}{\text{Area}_{\text{CH}_3}(\delta)} \quad (1)$$

where $\text{Area}_{\text{CH}_2\text{Cl}}$ and $\text{Area}_{\text{CH}_3}$ represent the integral area of CH_2Cl and CH_3 groups, respectively.

The membrane morphologies and microstructures was observed by scanning electron microscopy (SEM, Quanta 200). The surface-section and cross-section of membranes were sputtered with gold before observation.

2.3.2. Ion exchange capacity

IEC of the AEMs was determined with the classical Mohr method [29]. Firstly, the membrane samples (Cl⁻ form) were dried at 60 °C under vacuum for 24 h. They were then immersed in 30 mL of 0.5 mol/L Na_2SO_4 for 24 h to convert to the SO_4^{2-} form. The resulting solution was titrated with 0.1 mol/L AgNO_3 aqueous solution and using K_2CrO_4 as an indicator. IEC value of the AEMs was obtained according to the following equation:

$$\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{m} \times 100\% \quad (2)$$

where m is the weight of dry membrane; V_{AgNO_3} and C_{AgNO_3} represent the consumed volume and concentration of the AgNO_3 solution, respectively.

2.3.3. Water uptake, swelling ratio, and tensile strength

WU and swelling ratio (SR) were obtained by measuring weight and three-dimension before and after hydration. The AEM samples (4 cm \times 1 cm) were dried at 60 °C under vacuum for 48 h and then immersed in deionized water at room temperature for 24 h. The mass and three-dimension of the samples were quickly measured after removal of surfaces water with filter papers. The WU and SR values were calculated as the follows:

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (3)$$

$$\text{SR} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (4)$$

where W_{wet} and W_{dry} are the mass of hydrated and dehydrated samples; L_{wet} and L_{dry} are the dimension of hydrated and dehydrated samples, respectively.

Hydration number (λ , the number of water molecules per quaternary ammonium group) was calculated as the follow:

$$\lambda = \frac{\text{WU} \times 1000}{\text{IEC} \times M_{\text{H}_2\text{O}} \times 100} \quad (5)$$

where $M_{\text{H}_2\text{O}}$ is the molar mass of water.

Tensile strength (TS) of fully hydrated QAPSU membranes in Cl⁻ form was analyzed by a universal tensile machine (CM4104, Shenzhen SANS Testing Machine Co. Ltd., China) at a tensile speed of 5 mm/min with the samples of 1 cm \times 4 cm.

2.3.4. Membrane area resistance and transport number

R_m measurement of QAPSU membranes was carried out by Metrohm Autolab with the AC impedance method [30]. The membrane samples (3 cm \times 3 cm) were immersed in a 0.5 mol/L NaCl solution to reach the equilibrium condition for 48 h before testing. One membrane sample was used to separate a cell into two compartments (Fig. 1), and each compartment had 100 mL 0.5 mol/L NaCl solution. R_m was calculated by the following formula:

$$R_m = (R_{m1} - R_{m2}) \times S \quad (6)$$

where R_{m1} and R_{m2} are the resistances of the entire cell with and without membrane, respectively; S is the effective membrane area (3.14 cm^2).

Transport number (t) of QAPSU membranes was calculated by the same device in Fig. 1, the only difference was using constant current (supplied by Lodestar LP6002D generator) instead of alternating

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