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Preparation of monovalent cation selective membranes through annealing treatment



Liang Ge, Liang Wu, Bin Wu, Guanhua Wang, Tongwen Xu*

CAS Key Laboratory of Soft Matter Chemistry, Lab of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

Different from enhancing permselectivity of cation exchange membrane (CEM) by the common surface modification, this study reports an annealing treatment strategy to enhance the density of PVA-based CEM by tuning crystallinity, which can improve pore-size sieving effect for ions. X-ray diffraction (XRD) suggests that these membranes possess controllable crystallinity ranging from 11.8% to 43.9%. AFM analysis implies that after annealing treatment crystalline regions increase remarkably and distribute uniformly in membrane. When they are applied to electrodialysis (ED) for acid recovery from H^+/Zn^{2+} solution, it is experimentally evidenced that the permselectivity ($P_{H^+}^{Zn^{2+}}$) and Zn^{2+} leakage are dependent on crystallinity. The optimal membrane with a crystallinity of 43.9% exhibits a favorable permselectivity of 0.007 between Zn^{2+} and H^+ and only 0.01% of Zn^{2+} leakage, which are better than that of monovalent cation exchange membrane modified by surface modification.

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1. Introduction

As a result of extensive studies, the application of ion exchange membranes in separation ion species deserves much attention [1]. Especially, the separation of ions with different valence via ED is a currently hot topic which is concerned with many industries such as waste water treatment, hydrometallurgy, desalination of sea water, and so on. In these cases, the used membranes must be monovalent ion-selective besides the requirements of their intrinsic properties and stabilities.

Generally, surface modification is an effective method to improve the monovalent ion selectivity of ion exchange membranes [2–11]. In the case of the monovalent cation selective membrane, surface modification involves the formation of a dense cationic charged layer onto the membrane surface by electro-adsorption or chemical bonding. For example, polyethyleneimine [12] and quaternized chitosan [5] layer were attached to the membrane surface by electro-adsorption. They exhibit favorable monovalent ion selectivity, but the long time stability of the electrostatic bonded layer during the ED process is still in debate [13]. Surface modification by chemical bonding is a promising method to improve the stability behavior of the cationic charged layer during the ED process. Le et al. [2] have

proposed a diazonium-induced anchoring process to graft covalently a thin polyaniline-like layer on the surface of commercial cation exchange membrane (CEM). The experimental results showed that the covalently bonded layer can effectively block nickel ions. However, there is a long way for commercialization for such membranes and far away from industrial applications, because of the complication in preparation procedure and difficulty in process control.

Different from the previous reported strategy about formation of a dense cationic charged layer by chemical modification, this study presents an annealing treatment strategy to enhance the density of PVA-based CEM by tuning crystallinity. Due to the semi-crystalline nature of PVA, crystallinity of membranes can be deliberately controlled by adjusting annealing temperature. System of H_2SO_4 and $ZnSO_4$ will be used to test the membrane performance. The resultant membranes with the improved crystallinity are expected to exhibit the high monovalent cation selectivity during the ED process due to the pore-size sieving effect. The relationship among the annealing temperature, crystallinity, structures and separation properties of membranes will be discussed in detail.

2. Experimental

2.1. Materials

Anion exchange membranes (AEMs) made of polyvinylidene fluoride with ion exchange capacity of 1.6 mmol/g, were kindly

* Correspondence to: University of Science and Technology of China, Department of Chemistry, Jinzai Road 96#, Hefei, Anhui 230026, PR China.
Tel.: +86 551 6360 1587; fax: +86 551 63602171.

E-mail addresses: liangwu8@ustc.edu.cn (L. Wu), twxu@ustc.edu.cn (T. Xu).

supplied by Chemjoy Polymer Co. Ltd. of Hefei. Polyvinyl alcohol (PVA), with average degree of polymerization 1750 ± 50 , was supplied by Shanghai Yuanli Chemical Co. (China). Sodium styrene sulfonate (SSS) was purchased from Zibo Xingzhilian Chemistry Co. (China) and γ -methacryloxypropyl trimethoxy silane (γ -MPS) was from Nanjing Chuangshi Chemistry Co. Ltd. (China). The other reagents were of analytical grade and used as received. Azobisisobutyronitrile (AIBN) was dissolved in warm methanol (35 °C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature.

2.2. Membrane preparation

The detailed procedure for the preparation of PVA-based CEM is described in previous report [14]. In brief, 0.05 mol SSS and 0.01 mol γ -MPS were dissolved in 200 mL DMF under stirring at room temperature, and heated to 70 °C. Then 1.6% AIBN (with respect to the total molar amount of SSS and γ -MPS) was added to initiate polymerization reaction for 12 h. Consequently, a homogeneous and transparent copolymer solution was obtained. This solution (4.8 g) was then dropped into PVA solution (4 g) within 1 h, and the mixture was stirred at 60 °C for 18 h. Subsequently, the mixture solution was coated onto a glass plate, dried at room temperature for 2 days. After peeling off from the glass plate, a transparent and flexible membrane was obtained.

2.3. Annealing treatment

The obtained PVA-based CEM was heated from 25 °C to an annealing temperature for 1 h, and kept at the annealing temperature for 1 h. Then the temperature was cooled at the rate of 10 °C/h. The pristine membrane without annealing treatment was signed as M, and the membranes were annealed at 120 °C, 140 °C, 160 °C, and 180 °C signed as M-120, M-140, M-160, and M-180, respectively.

2.4. Membrane characterization

Ion exchange capacity (IEC) was measured through conventional titration. The membrane in the H^+ form was converted to the Na^+ form after immersing in a NaCl aqueous solution (0.5 mol dm^{-3}) for 8 h. The H^+ ions released from the membrane were titrated with a 0.01 mol dm^{-3} NaOH aqueous solution. The IEC values were calculated from the released H^+ ions and expressed as mmol g^{-1} of dry membrane.

Water uptake (WU) was measured to investigate the membrane hydrophilicity. The dry membrane samples were weighed and immersed in distilled water at 25 °C for 2 days. Surfaces of the wet samples were then carefully dried and the samples were weighed. WU was calculated as follows:

$$WU = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

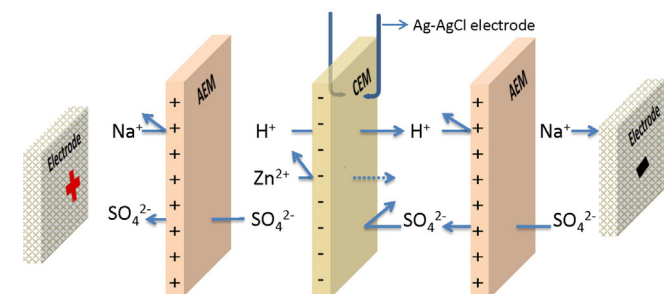


Fig. 1. Electrodesialysis cell for separation tests.

where W_d is the dry weight of the membranes and W_w is the wet weight of the membranes after immersion in distilled water at 25 °C.

The tensile properties were measured on an Instron universal tester (Model 5900) at 25 °C with dumbbell shaped specimens and a crosshead speed of 10 mm min^{-1} . Measurements were taken on samples immediately removed from water after being soaked for at least 24 h. The tensile strength (TS) and elongation at break (E_b) values were recorded.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) analyses were performed with a Thermo Nicolet FT-IR spectrometer/analyzer model 6700, using an IR source and a MCT/B detector. Due to the low reflection of membranes, the multi-reflection method, using a ZnSe/45° ATR plate, was preferred. Data were recorded, under low pressure, between 500 and 4000 cm^{-1} .

The crystalline structure of membranes was tested using X-ray diffraction (XRD) in the range of 10–40° and at the speed of 2° min^{-1} (Rigaku D/max 2500 v/pc, CuK 40 Kv, 200 mA).

Tapping mode atomic force microscopy (AFM) observations were performed with a veeco dilnnova SPM, using micro-fabricated cantilevers with a force constant of approximately 20 N m^{-1} .

2.5. Electrodesialysis tests

ED was performed in a four-compartment cell (Fig. 1). The different compartments were separated by two anion exchange membranes (AEM) facing the electrodes and the CEM under study. The apparent area of the membrane was 7.07 cm^2 . Two disks, which were made of titanium coated with ruthenium, were used respectively as the anode and cathode electrodes. The dilute compartment contained 250 cm^{-3} of $0.23 \text{ mol dm}^{-3} \text{ Zn}^{2+}$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ while the concentrate compartment contained 50 cm^{-3} of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The catholyte and the anolyte contained 100 cm^{-3} of $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, respectively. A current of 30 mA cm^{-2} was applied through the system for 1 h using a direct current power supply.

The flux of an ion i is defined by

$$J_i = \frac{t_i j}{z_i F} \quad (2)$$

where z_i is the valency of ion i , $J_i/\text{mol cm}^{-2} \text{ s}^{-1}$ is its unidirectional flux, $j/\text{mA cm}^{-2}$ is the applied current density and F is the Faraday constant.

Permselectivity and Zn^{2+} leakage were used to evaluate the efficiency of the annealing treatment. The permselectivity between Zn^{2+} and H^+ was calculated as follows:

$$p_{H^+}^{\text{Zn}^{2+}} = \frac{t_{\text{Zn}^{2+}}/2C_{\text{Zn}^{2+}}}{t_{H^+}/C_{H^+}} \quad (3)$$

which is called the transport number of Zn^{2+} ions relative to H^+ , where $t_{\text{Zn}^{2+}}$ and t_{H^+} are the transport numbers of Zn^{2+} and H^+ in membranes, respectively, and $C_{\text{Zn}^{2+}}$ and C_{H^+} are the concentrations of Zn^{2+} and H^+ at the desalting side solution during electrodesialysis, respectively. And Zn^{2+} leakage was calculated as follows:

$$\text{Zn}^{2+} \% = \frac{\text{mass of Zn}^{2+} \text{ in concentrated cell}}{\text{mass of Zn}^{2+} \text{ in concentrated cell and dilute cell}} \times 100 \quad (4)$$

Membrane area resistance was measured using the same apparatus. A digital multimeter was used to record the voltage drop, when a very low current pass through the apparatus. The area resistance of the membrane was determined by the difference

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