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Cation exchange membranes from hot-pressed electrospun sulfonated poly(phenylene oxide) nanofibers for alkali recovery

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ABSTRACT

Cation exchange membranes (CEMs) have been prepared from sulfonated poly(phenylene oxide) (SPPO) by electrospinning and hot-press treatment. Effect of various parameters, such as concentration, voltage and tip to collector distance (TCD) as well as the hot-press treatment conditions on properties of membrane has been fully investigated. When being applied in diffusion dialysis (DD) for alkali recovery from Na_2WO_4/NaOH solution, the membrane exhibits higher hydroxide permeability (U_{OH}, 0.00971 m/h) and separation factor (S, 36.09) than the solution casting SPPO membrane (CSPPO), of which U_{OH} is only 0.00605 m/h and S is 21.8. Compared with previously reported DD membranes with U_{OH} in the range of 0.0014–0.0022 m/h, Hot-pressed Electrospun SPPO (H-ESPPO) shows *approx.* 4 times higher in U_{OH}, underling its superior performance in DD application.

1. Introduction

Diffusion dialysis (DD), a ion-exchange membrane separation process utilizing the concentration gradient as driving force [1], has attracted great attentions in water treatment for its environmentally-friendly and low cost energy consumption (renewable energy). Up to now, DD is widely used in acids recovery, such as hydrochloric acid, sulfuric acid and lactic acid, etc. [2–5]. Alkali recovery is equally significant to enhance the value of recycling alkaline and can bring great environment and economic benefits to enterprises. During the alkaline DD process, CEMs play an important role in the sodium ions transport by the concentration gradient between the feed and permeate sides [6]. Nevertheless, due to the lack of high performance cation exchange membranes (CEMs), DD for alkaline water treatment (for example, Na_2WO_4/NaOH mixture), has been rarely reported [7]. In order to expand the application field of DD to alkaline treatment, the availability of suitable CEMs becomes an important factor. To achieve high performance for DD, CEMs should not only possess high OH^- permeability, strong rejection of acid radical anions (such as WO_4^{2-}) and low water permeability but also outstanding thermal/chemical stability as well.

Besides inherent properties of the materials, membrane properties largely depend on preparation techniques. The commercial CEMs (e.g., Neosepta-CMX from Astom Corp., Tokyo) developed for electrodialysis do not meet the requirements for DD application due to the low permeability resulted from their compact structure [8]. Up to date, the directly casting method is the main approach to prepare CEMs for DD. A series of organic–inorganic hybrid CEMs have been developed using this method. Micro-separation between the organic and inorganic phases, leads to a relatively loose morphology, which is in favor of hydroxide ions permeating through membrane. [6,8–13]. However, the hybrid CEMs usually exhibit poor mechanical properties due to the fragile silica component, which will limit its practical application.

In recent years, a new preparation method of ion-exchange membranes based on electrospinning deposition has attracted wide attentions in scientific research [14–16]. It is a versatile and well-developed technology for the production of non-woven nanofiber mats with nano-scale diameters. The nanofiber mat not only have the extremely small fiber diameters from nano- to sub-micron range, but also have fairly higher tensile modulus in individual fibers compared with the bulk [17,18]. After hot-press treatment, the membranes can be easily obtained with a dense structure in a macroscopic scale but loose structure in a microscopic scale. Obviously, the micro-scale loose morphology will impart the CEM high permeability and proper selectivity for alkaline recovery as that of organic–inorganic hybrid CEM, but better flexibility due to the absence of the inorganic component.

Hence, our current efforts aim to develop novel CEMs through the direct electrospinning of SPPO nanofibers followed by hot-press treatment and investigate their performances in DD process.

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To the best of our knowledge, this is the first systematic study on electrospinning of cation-containing polyphenylene oxide, also the first electrospun CEM applied in DD process. To optimize the properties of the electrospun membranes, the various parameters, such as concentration, voltage and tip to collector distance (TCD) as well as the hot-press treatment conditions on the final membrane were fully investigated. Alkali recovery of optimized membranes was investigated by DD test. Here, Na_2WO_4/NaOH mixture was chosen as the model alkali waste solution with a strong background of waste treatment in tungsten ore smelting industry which generally produces a large amount of waste containing OH^- and WO_4^{2-}.

2. Experimental

2.1. Materials

Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) in Na^+ form was kindly supplied by Tianwei Membrane Co. Ltd. (Shan-dong, China) with ion exchange capacity around 2.1 mmol g^{-1} dry. Dimethyl formamide (DMF) is of analytical grade and obtained from China National Medicines Corporation Ltd. Deionized water was used throughout. The other reagents are of analytical grade and used as received.

2.2. Preparation of electrospun SPPO membranes

Electrospun SPPO membranes (ESPPO) were prepared by electrospinning purified SPPO solution using DMF as the solvent. Standard electrospinning equipment obtained from Yongkang leye (Beijing, China) was used. For the membrane preparation, the following process steps were undertaken: SPPO was dissolved in DMF under constant stirring at room temperature for 24 h in order to get a homogeneous solution. 2 ml disposal with 22 gauge metal needle (inner diameter=0.394 mm) was used and its injecting rate was 0.1 mm/min. A voltage of −1 kV and 17.0 kV was applied to the tip and the collector respectively, with a distance of 17 cm at ambient temperature. The nanofibrous SPPO mats, which are referred to as Electrospun SPPO (ESPPO), were collected on the drum collector at the desired thicknesses of 120–160 μm and dried in a vacuum oven for 12 h. Subsequently, the nanofibrous mats were treated with DMF atmosphere (35 °C) for 15 min, and then hot-pressed at a working pressure of 14 MPa at 120 °C to get comparatively dense SPPO membranes. The final heat-press electrospun SPPO membranes with the thickness in the range of 50–70 μm were named as H-ESPPO membranes. For comparison, SPPO membrane was also prepared using a conventional casting method, i.e., 15% homogeneous solution of SPPO in DMF was cast on a clean glass plate with a desire thickness and then dried in a vacuum oven at 60 °C. The final casting SPPO membrane was named as CSPPO membrane.

2.3. Membrane characterizations

The ion exchange capacity (IEC) was measured by classical titration as follow: dry SPPO membrane was sampled, accurately weighed and converted to H^+ form in 1.0 mol/L HCl for 48 h at room temperature. Excess HCl was washed off and the sample was then immersed in 1 mol/L NaCl for 2 days. IEC was obtained by determining the content of HCl through titration with 0.04 mol/L NaOH.

Water uptake (WU) was measured according to the hydrophobicity of the membranes. The membranes were dried in oven at 50 °C for 10 h and weighed. They were then immersed in deionized water for 24 h and weighed after removal of the surface water. The value of WU was calculated through the relative weight gain per gram of the dry sample.

A Shimadzu TGA-50H analyzer was used for TGA. Derivatograms of the TGA curves (DTG) were recorded under nitrogen purge with a heating rate of 10 °C/min. The short-term thermal property and stability of the polymer will be indicated by this technique.

The tensile strength (TS) and elongation at break (E_b) values were recorded on an Instron universal tester (Model 1185). The tensile analyses were accomplished at 25 °C with dumbbell shaped specimens and a crosshead speed of 25 mm/min with an initial gauge length of 25 mm.

The N_2 adsorption–desorption isotherms were measured in a Micromeritic Tristar II 3020 M apparatus. The sample was degassed under high vacuum until the vacuum to 10^{-3} mmHg at 373 K. The N_2 isotherms were obtained at 77 K, and analyzed by the Brunauer–Emmett–Teller (BET) method.

For the estimation of alkaline stability, the membrane was treated with an aqueous NaOH solution (1 mol/L) at room temperature for increasing lengths of days, and then, water was quickly removed from the surfaces and the mass of the samples were measured, respectively.

2.4. Diffusion dialysis test

The DD test has been carried out through the same set-up as previous described in [19] and is only briefly summarized here: The membrane sample with an effective area of 5 cm^2 was fastened between a two-compartment cell. One side was filled with the mixed solution of NaOH and Na_2WO_4, and the other with distilled water. The concentrations of NaOH and Na_2WO_4 were chosen according to our previous work [20]. To minimize concentration polarization effects during the diffusion test, both compartments were stirred at identical rate.

The diffusion process was allowed for 60 min before the permeate/diffusate solutions being transferred to the corresponding beaker. Then the OH^- concentrations in permeate/diffusate solutions were determined by titration with HCl solution, while the WO_4^{2-} concentration in the diffusate solution was determined by ultraviolet spectrophotometry [7].

The separation factor (S) with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be calculated by the following formula [21]:

$$U = \frac{M_m}{At\Delta c} \tag{1}$$

where M_m is the amount of components transported in moles, A the effective area in square meters, t the time in hours, and Δc the logarithm average concentration between the two chambers in moles per cubic meters. Δc is defined as below

$$\Delta c = \frac{c_f^0 - (c_f c_d)}{\ln [c_f^0/(c_f c_d)]} \tag{2}$$

where c_f^0 and c_f are the feed concentrations at time 0 and t, respectively, and c_d the dialysate concentration at time t [22].

3. Results and discussions

3.1. Optimization of electrospinning conditions

In order to prepare excellent electrospun fibers with bead-free and uniform structure, polymer solutions require sufficient chain overlap and entanglements to generate sufficient viscosity [21]. During the experiments, the influence of various parameters on