

Characterization of cation-exchange membranes prepared from a graft-copolymer consisting of a polysulfone main chain and styrene sulfonic acid side chains



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ABSTRACT

The cation-exchange membranes (CEMs) were prepared from a graft-copolymer consisting of a polysulfone (PSF) main chain and styrene sulfonic acid side chains. The graft-copolymer was synthesized by grafting ethyl *p*-styrenesulfonate (Etss) on macro-initiators of chloromethylated polysulfone with different contents of chloromethyl (CM) groups, changing Etss content in the polymers by using atom transfer radical polymerization. The PSF based-CEMs show almost the same mechanical strength as commercially available CEMs. The CEMs with CM content = 16.6 mol% have higher transport properties (dynamic state transport number = 0.98, membrane resistance = 1.5 Ω cm²) than commercially-available CEMs.

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1. Introduction

Water shortages in the developing countries are one of problems worldwide [1]. Therefore, demands in desalination of brackish water and seawater by electrodiaylsis (ED) system (Fig. 1) has increased one of the technologies to overcome the problems. In an ED desalination process, cations and anions in the desalination compartments in the system are transported through cation-exchange membranes and anion-exchange membranes, respectively, to the concentrated compartments by electrical potential difference between the membrane surfaces as the driving force. The advantages of ED desalination processes compared with other membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are high water recovery, less raw water pretreatment and the possibility to operate at temperatures of up to 50 °C [2]. This process has been widely used for production of drinking water, treatment of medical supplies, treatment of industrial effluents, food industry, and acid recovery from pickling solutions [3–10].

In Japan, hydrocarbon-type ion exchange membranes (IEMs) have been developed to produce NaCl by electrodiaytic concentration of seawater. Neosepta IEMs (ASTOM Corp. Japan) are one of the most popular hydrocarbon-type IEMs [11]. The IEMs in the ED process are expected some characteristics: high permselectivity; low membrane resistance; high chemical stability; high mechanical strength [12]. Recently, almost all commercial IEMs are prepared by a paste method [13,14]. The drawbacks of the paste method are high production cost and low durability at high temperatures due to the support clothes made from polyvinyl chloride.

In previous studies [15–17], we designed graft-copolymers consisting of two chemically different polymer segments: a main chain made from a polymer having a high glass transition temperature (T_g) for high mechanical strength, and side chains made from a polymer having a conductive properties. Fig. 2 shown proposed structure of a cation-exchange membrane (CEMs) prepared from the graft-copolymer and the polymer structure of the graft-copolymer.

In this study, a graft-copolymer for high performance CEMs having high cation permselectivity, low membrane resistance as well as high mechanical strength was synthesized. The polymer was prepared by grafting styrene sulfonic acid monomers on a chloromethylated PSF as a macro-initiator of atom transfer radical polymerization (ATRP) [18,19]. ATRP for the polymerization of

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c_{K^+}	The concentration of K^+ ions in the solution, mol/dm^3
c_{Etss}^m	Etss content in feed, wt %
c_{CM}^p	CM content in the macro-initiator, mol %
IEC	Ion exchange capacity, meq g^{-1} dry membrane
F	Faraday constant, C mol^{-1}
q	Amount of electricity, C
R_m	Membrane resistance, $\Omega \cdot \text{cm}^2$: $R_m = R_1 - R_0$
R_s	Measured resistance with a sample membrane, $\Omega \cdot \text{cm}^2$
R_0	Measured resistance without a sample membrane, $\Omega \cdot \text{cm}^2$
t_+	Transport number, -
V	Volume of the measurement solution, dm^3
W	Water uptake, wt%
W_w	Weight in wet state, g
W_D	Weight in dry state, g
Δm	Amount of transported ions passed through the membrane, mol
Δc	The concentration change of the transported ions, mol/dm^3

various monomers has been developed by Matyjaszewski and co-workers [20,21]. Chloromethylation has been one of the modification of polymers because of its versatility and good reactivity. Chemical structure of the graft-copolymer is shown in Fig. 2 (b). The CEMs with various ion exchange capacity (IEC) prepared from the graft-copolymers was investigated the effect of IEC on membrane properties for electrodialysis namely, the membrane resistance, dynamic state transport number and mechanical strength.

2. Experimental

2.1. Synthesis of chloromethylated PSF (CM-PSF) as a macro-initiator for ATRP

Zinc oxide (ZnO: Wako Pure Chemicals Ind., Ltd) was dissolved in chloromethylmethylether (CMME: Tokyo Chemical Industry

Co., Ltd) in a 300 mL, three-necked round-bottom flask equipped with a condenser and a dropping funnel. PSF ($M_w = 35,000$ g/mol, 75,000 g/mol: Sigma-Aldrich Chemical Co., Ltd) was dissolved in 100 mL of dichloroethane (CH_2Cl_2 : Wako Pure Chemicals Ind., Ltd.). The solution was slowly added to the reaction mixture in the three-necked round-bottom flask using the dropping funnel. The mixture was stirred under nitrogen at 50°C at different allocated time interval and then poured into 1000 mL of methanol. The precipitate was filtrated and dried under reduced pressure at 80°C for at least 24 h.

2.2. Synthesis of graft-copolymers using ATRP

The CM-PSF was dissolved in 1-methyl-2-pyrrolidinone (NMP: Sigma-Aldrich Chemical Co., Ltd) at room temperature and then the various amounts of *p*-ethyl styrenesulfonate (Etss) (Tosoh Co., Ltd.) were added to the solution. The mixtures were purged with nitrogen gas and stirred for 30 min and then copper (I) chloride (CuCl : Sigma-Aldrich Chemical Co., Ltd.) and 4,4'-dimethyl-2,2'-dipyridyl (bpy: Sigma-Aldrich Chemical Co., Ltd.) were added. The reaction was carried out at 90°C for 48 h. After polymerization, the resultant mixtures were precipitated into a petroleum ether/ethanol/HCl solvent. The obtained graft-copolymers were dried in vacuum at 80°C to constant weight.

2.3. Preparation of CEMs

Precursor membranes were prepared by casting a NMP solution of the graft-copolymers on teflon sheet and drying in vacuum at 80°C for 24 h. CEMs were prepared by immersing the precursor membranes in hot water (95°C) for 24 h to remove the ethyl groups of Etss by hydrolysis reaction.

2.4. Analysis of chemical structure

Nuclear magnetic resonance (NMR) spectra were performed on the PSF, the macro-initiators and the graft-copolymers using a spectrometer for ^1H (JEOL JNM-EX270FT NMR system). CDCl_3 and $\text{DMSO}-d_6$ was used as the solvent and tetramethylsilane as an internal standard. The data were analyzed using commercially available software (JEOL DATYIM LTD. ALICE2) to estimate the chloromethyl

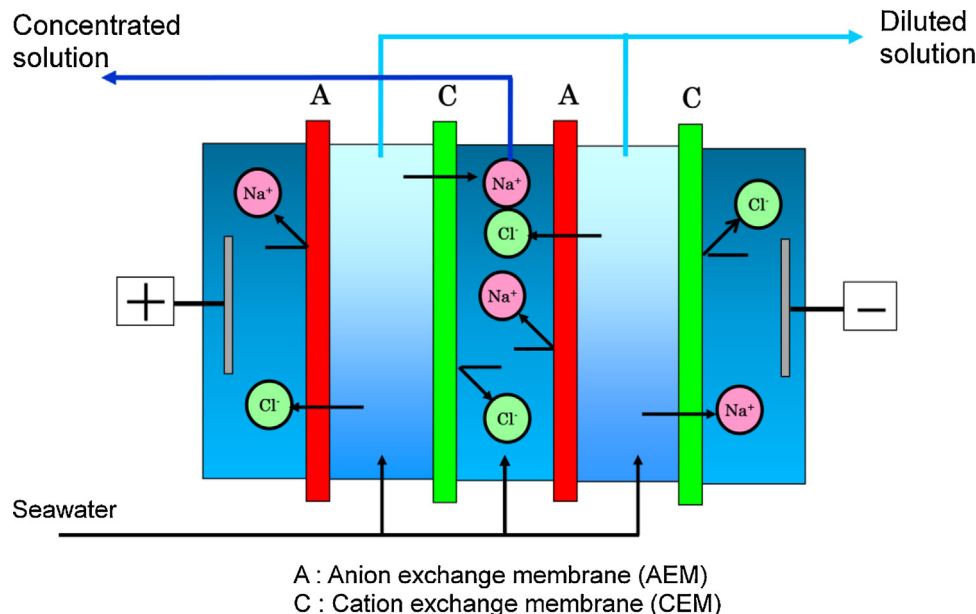


Fig. 1. Schematic diagram of electrodialysis system.

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