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Preparation and electrochemical characterizations of anion-permselective membranes with structurally stable ion-exchange sites

Yong-Jin Choi[a,*], Jee-Hye Song[a], Moon-Sung Kang[b,*], Bong-Kuk Seo[c]

[a] *Department of Chemical Engineering, Dong-eui university, Busan, 614-714, South Korea*
[b] *Department of Environmental Engineering, Sangmyung University, Cheonan, Chungnam, 330-720, South Korea*
[c] *Korea Research Institute of Chemical Technology, Daejeon, 305-600, South Korea*

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ABSTRACT

Novel semi-interpenetrating polymer network (semi-IPN) anion-permselective membranes are prepared *via* a facile monomer sorption method. The base membrane is prepared by *in-situ* copolymerization of *N*,*N*'-dimethylaminoethyl methacrylate (DMAEMA) and divinylbenzene (DVB) in a non-porous poly(vinyl chloride) (PVC) substrate film (*i.e.* poly(DMAEMA-*co*-DVB)/PVC). The successive quaternization reaction along with di-functional *p*-xylylene dichloride forms the structurally stable anion-exchange groups that are fused with one another. Various characterizations (measurements of the transport number, electrical resistance, *I-V* curves, and chronopotentiometry etc.) reveal that the electrochemical properties of the prepared membranes are almost comparable with those of a commercial anion-exchange membrane (AMX, Astom Corp., Japan). In addition, the structural stability of the anion-exchange sites is confirmed through the water-splitting experiments at a high applied current condition.

1. Introduction

Ion-permselective ionomer membranes are currently widely used in many water treatment applications such as the diffusion dialysis [1–5], electrodialysis [6–9], and capacitive deionization [10–12] for the desalination of brackish water, production of table salt, recovery of valuable metals from the effluents of metal-plating industry, and recoveries of acid and base from the spent leaching solutions etc. Recently, the ionomer membranes are also utilized in various energy devices such as fuel cells [13–17], reverse electrodialysis [18,19], and redox flow batteries [20–22]. In addition, alkaline water electrolysis employing anion-exchange membranes (AEMs) has been attracting considerable attention lately owing to its merits of cost-effective and efficient hydrogen production [23–25].

The emergence of new applications, therefore, have encouraged the development of novel ion permselective membranes with both excellent properties and high cost-effectiveness better than those of the conventional membranes synthesized *via* various techniques, *e.g.* bulk polymerization [26], latex [27], polymer blending [28], and paste methods [29,30]. Meanwhile, we have previously reported the preparation of ion-exchange membranes based on semi-interpenetrating polymer network (semi-IPN), which were simply prepared by absorbing monomer components into a supporting film (*e.g.* non-porous polyvinyl chloride) ("monomer sorption method") [31–34].

Although a wide range of preparatory methods for ion-exchange membranes have been developed, most of the AEMs are still vulnerable to harsh external conditions determined by an applied current or a type of solution [35]. For example, quaternary amonium salts, which are generally used as anion-exchange sites, are also easily decomposed due to their intrinsic structual instablity [35]. These drawbacks have seriously limited the long-term utilization of the membranes in an electro-driven process such as alkaline water electrolysis. Therefore, the objectives of this study are to 1) synthesize high performance anion-exchange membranes with structurally stable ion-exchange sites and to 2) investigate their electrochemical properties for the applications to various electro-driven processes. Novel semi-IPN membranes based on poly(*N*,*N*'-dimethylaminoethyl methacrylate-*p*-xylylene dichloride) that contain structurally stable anion-exchange sites have been successfully prepared *via* a monomer sorption method. In addition, both the morphological and electrochemical properties of the prepared anion-exchange membranes have been systematically investigated through various analyses.

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* Corresponding authors. Tel.: +82 41 550 5383; fax: +82 41 550 5313.
E-mail addresses: yjchoi64@deu.ac.kr (Y.-J. Choi), solar@smu.ac.kr (M.-S. Kang).

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2. Experimental

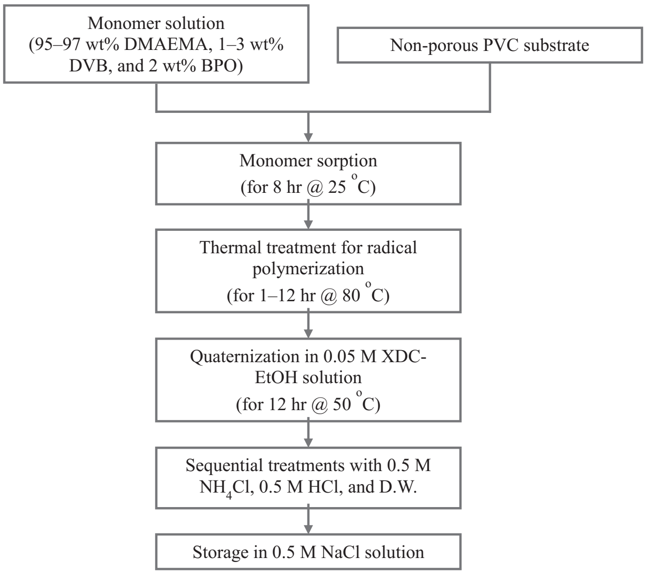
2.1. Materials and membrane preparation

Non-porous polyvinyl chloride (PVC) film with a thickness of *ca.* 150 μm (supplied from LG Chem. Co., Korea) was used as the supporting material. *N*,*N*'-Dimethylaminoethyl methacrylate (DMAEMA, Sigma–Aldrich Co., USA) was purified to remove inhibitors with an inhibitor-removal column before use. In order to remove inhibitors, divinylbenzene (DVB, 80% purity with mixture of isomers, Sigma–Aldrich Co., USA) was also purified, without the separation of isomers, by treating with 10 wt% sodium hydroxide aqueous solution and then washed with distilled water several times. *p*-Xylylene dichloride (XDC, Sigma–Aldrich Co., USA) for the quaternization of the polymer was used as received. After drying with anhydrous calcium sulfate overnight, DMAEMA and DVB were fractionally distilled under vacuum. Benzoyl peroxide (BPO, Tokyo Kasei, Co., Japan) was purified by recrystallization in a methanol/water mixture at −5 °C. Neosepta® AMX membranes (Astom Co., Japan) were used as the reference to compare with the membranes prepared in this study.

The schematic flow diagram of the membrane preparation process is illustrated in Scheme 1. Monomer solutions consisting of 95–97 wt% DMAEMA, 1–3 wt% DVB, and 2 wt% BPO were prepared to synthesize the base membrane. A non-porous PVC film was immersed in a monomer solution at room temperature for 8 h (for the monomer sorption) and then placed between two glass plates and sealed with polypropylene tape to prevent any loss of the monomers through evaporation. More detailed polymerization conditions have been described elsewhere [32]. The polymerization ratio of the base membrane was evaluated by the weight gain (WG) of the film during the polymerization according to the following equation:

$$WG = \frac{W_P}{W_{PVC}} \tag{1}$$

where W_P is the weight of poly(DMAEMA-*co*-DVB) (=membrane weight after polymerization – W_{PVC}) (g) and W_{PVC} is the weight of PVC substrate (=membrane weight before polymerization) (g). The polymerized base membrane was then immersed in a 0.05 M XDC-EtOH solution overnight at 50 °C for quatenization, followed by sequential treatments with 0.5 M NH_4Cl, 0.5 M HCl, and ultrapure water. The prepared membranes were stored in 0.5 M NaCl solution before use.



Scheme 1. Schematic representation of the membrane preparation process.

2.2. Characterizations

The polymerized structure of the prepared membranes was confirmed by FT-IR/ATR (460 plus, Jasco, Japan). Morphological features of the as-prepared membranes were also evaluated using field emission scanning electron microscopy (FE-SEM, TESCAN, Czech) and differential scanning calorimeter (DSC, TA Instruments, USA). To observe any change in the glass transition temperature (T_g), calorimetric measurements were carried out in a Perkin-Elmer DSC-1B apparatus. Thermograms were recorded for 3–4 mg of a sample under nitrogen flow ($10^{-5}\,m^3\,min^{-1}$) at a heating rate of $10\,°C\,min^{-1}$, from room temperature to -50–150 °C.

The water uptake (WU) was calculated by the following equation [6]:

$$WU = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100 \tag{2}$$

where W_{wet} and W_{dry} are the wet and dried membrane weights, respectively.

The ion-exchange capacities (IECs) of the AEMs were determined through the conventional method [16]. After the membrane is equilibrated with 0.5 N NaCl solution, excess Cl^- ions in the membrane are removed with distilled water. The ion-exchanged Cl^- ions in the membrane are eluted in a Na_2SO_4 solution and then quantified by a titration with $AgNO_3$ (the Mohr method) using the following equation:

$$IEC = \frac{N_{cl^-,sample} \cdot V_{sample}}{W_{dry}} \tag{3}$$

where $N_{Cl\text{-},sample}$ is the normal concentration of Cl^- ions (mili-equivalent/L) and V_{sample} is the volume of the sample solution containing Cl^- ions (L).

The membrane electrical resistances (MER) were determined using a lab-made clip cell and an LCZ meter (at a frequency of 10^5 Hz). The magnitude of impedance ($|Z|$) and the phase angle of impedance (θ) of a membrane were measured and converted into MER ($\Omega\,cm^2$) value using the following equation [6]:

$$MER = \left(|Z|_{sample} \cdot \cos\theta_{\text{sample}} - |Z|_{blank} \cdot \cos\theta_{\text{blank}}\right) \times area. \tag{4}$$

The apparent transport number of the counter ion in the prepared membranes was determined by the *emf* method using a pair of Ag/AgCl electrodes and a two-compartment cell (each volute: 230 mL) [6]. The anion transport number ($\overline{t_-}$) for each membrane was calculated by the following equation [16]:

$$E_m = \frac{RT}{F}(1 - 2\overline{t_-})\ln\frac{C_1}{C_2} \tag{5}$$

where E_m is the cell potential, R the molar gas constant, T the absolute temperature, F the Faraday constant, and *C1* and *C2* are electrolyte concentrations in low (1 mM NaCl) and high (5 mM NaCl) concentration compartments, respectively.

Current-voltage (*I-V*) experiments were performed in a conventional two-compartment cell with a 0.025 M NaCl solution for both compartments. The schematic diagram of two-compartment electrolytic cell used for the *I-V* experiments is shown in Fig. 1. For the measurement, a pair of Ag/AgCl reference electrodes was positioned at both membrane and then potential was swept from 0 to 4.2 V at a scan rate of $10\,mV\,s^{-1}$ between a pair of Ag/AgCl plate electrodes. In addition, chronopotentiometry was performed with an Ag/AgCl reference electrode and two Ag/AgCl plates at a constant current of 3.5 mA for duration of 100 s to obtain a