



Facile surface modification of anion-exchange membranes for improvement of diffusion dialysis performance



Do-Hyeong Kim^a, Han-Sol Park^a, Seok-Jun Seo^a, Jin-Soo Park^a, Seung-Hyeon Moon^{b,*}, Young-Woo Choi^c, Young Su Jiong^d, Dong Hee Kim^d, Moon-Sung Kang^{a,*}

^a Department of Environmental Engineering, Sangmyung University, 300 Anseo-dong, Dongnam-gu, Cheonan 330-720, Republic of Korea

^b School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Republic of Korea

^c Fuel Cell Research Center, Korea Institute of Energy Research, Yuesong-gu, Daejeon 305-343, Republic of Korea

^d ENERTEC Co. Ltd., 138 Gongdanbukgil, Chilseo-myeon, Haman-gun, Gyeongsangnam-do 637-941, Republic of Korea

ARTICLE INFO

Article history:

Received 30 July 2013

Accepted 8 October 2013

Available online 21 October 2013

Keywords:

Interfacial polymerization

Anion-exchange membranes

Polypyrrole

Diffusion dialysis

Surface modification

ABSTRACT

In this study, a facile membrane modification method by spin-coating of pyrrole (Py) monomers dissolved in a volatile solvent followed by an interfacial polymerization is proposed. The surface of a commercial anion-exchange membrane (i.e., Neosepta-AFX, Astom Corp., Japan) was successfully modified with polypyrrole (Ppy) to improve the acid recovery performance in diffusion dialysis (DD). The result of DD experiments revealed that both the acid and metal ion transports are significantly influenced by the surface modification. The metal crossover through the membranes was largely reduced while mostly maintaining the acid permeability by introducing a thin Ppy layer with excellent repelling property to cations on the membrane surface. As a result, the anion-exchange membrane modified with the optimum content of Py monomer (5 vol.%) exhibited excellent acid dialysis coefficient (K_{Acid}) and selectivity (K_{Acid}/K_{Metal}) which is approximately twice as high as that of the pristine membrane.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Diffusion dialysis (DD) is known as one of the attractive environmentally-friendly separation processes using ion-exchange membranes [1–4]. It is advantageous in its low energy consumption since it is driven by a concentration gradient without the use of electrical energy except solution pumping. Since DD was reported by Graham as a method of separating small molecules from large ones, the technology was the first applied industrially in the late 1950s [5,6]. Up to now, it has been widely investigated for effective recoveries of acids and alkalis in waste discharges containing metal ions from the processes of resin regeneration, steel production, metal-refining, and aluminum etching [4–7].

There are two types of models to describe a DD permeation process such as the solution-diffusion model and the three-phase membrane model [4,8]. The former explains the transport of dissolved components in a membrane phase with a concentration gradient, and the latter refers to the hopping mechanism of anions and the dragging mechanism of protons and other cations through active and interstitial regions in an anion-exchange membrane (AEM). Particularly, the exceptionally high proton mobility due to both diffusion and Grotthuss mechanism enables efficient acid

recoveries [1]. Furthermore, a theoretical understanding on the DD process has been studied by Nernst–Planck equation and Teorell–Meyer–Sievers [9], a lumped parameter model [10], various solution compositions by Palatý group [11–15], and systematical membrane studies by Xu group [4,16–21].

There have been several attempts to modify interfaces of ion-exchange membranes, improving the membrane properties such as the ion transport and selectivity. Sata et al. examined interactions between anionic polyelectrolytes and anion-exchange membranes in terms of selectivity and transport number [22]. In addition, modification of a cation exchange membrane was conducted using acid–amide bonding of polyethyleneimine to improve electrochemical properties [23,24]. Zeng et al. introduced polypyrrole (Ppy) coating at the interfaces of Nafion membranes [25]. Schwenzer et al. compared Ppy and polyaniline coatings on Nafion membranes in terms of transport properties. The nitrogen heteroaromatic pyrrole rings in Ppy become protonated under the strongly acidic conditions of the diffusion test solutions. Thus, Ppy was expected to form a cationic blocking layer for metal ions [26]. However, the effects of interfacial modifications of anion-exchange membranes have not been sufficiently investigated yet especially for DD applications. Anion-exchange membranes for DD applications are also expected to have larger free volume at which hydrated salts (co-ion and counter-ion) are allowed to be transported up to a certain level. It means that metal ions that

* Corresponding authors. Fax: +82 41 550 5313.

E-mail addresses: shmoon@gist.ac.kr (S.-H. Moon), solar@smu.ac.kr (M.-S. Kang).

are almost cationic could be diffused along with their co-ion as well as acid. It results in a decrease in acid selectivity and recovery efficiency.

The aim of this study is to improve DD performance by the surface modifications of a commercial anion-exchange membrane (i.e., Neosepta-AFX membrane, Astom Corp., Japan) with a polymer having the good repelling property to cations (i.e., Ppy). The electrochemical properties of the surface-modified membranes were systematically investigated by the measurements of I - V curve, chronopotentiometry, transport number, electrical membrane resistance, etc. Moreover, the dialysis coefficients of proton and iron species were evaluated and compared with those of the pristine membrane.

2. Experimental

2.1. Materials and membrane modification

A commercial Neosepta-AFX membrane was provided by Astom Corp., (Japan). Acetonitrile (ACN), pyrrole (Py), and iron (III) chloride were purchased from Aldrich (USA). All chemicals were of analytical reagent and used as received without further purification.

Ppy coating was carried out using various mixtures of Py and ACN in the volume ratio of 10:0, 8:2, 6:4, 4:6, 2:8, 1:9, and 0.5:9.5 to control the thickness. In this study, ACN was chosen as a solvent because of good miscibility with Py monomer and high volatility. Each mixture was spin-coated on a surface of the Neosepta-AFX membrane at a rotating speed of 2000 rpm for 1 min. Subsequently, the spin-coated membrane was immersed in a 0.2 mol dm^{-3} FeCl_3 aqueous solution for 5 min to form a thin Ppy layer on the membrane surface. The membranes were repeatedly washed with deionized water and immersed in 0.5 mol dm^{-3} NaCl for more than one day.

2.2. Membrane characterization

Surface images of the pristine and surface-modified membranes were examined by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700).

A membrane electrical resistance (MER) was measured using electrical impedance spectroscopy with a clip cell. Before the test, the samples were pre-equilibrated in a 0.5 mol dm^{-3} NaCl for more than one day. The magnitude of impedance ($|Z|$) and the phase angle of impedance (θ) of a membrane were measured and converted into MER ($\Omega \text{ cm}^2$) value using the following equation [27,28]:

$$MER = (|Z|_{\text{sample}} \cdot \cos \theta_{\text{sample}} - |Z|_{\text{blank}} \cdot \cos \theta_{\text{blank}}) \times \text{area}. \quad (1)$$

The apparent transport number of anion through the membranes was determined by the *emf* method using a two-compartment cell (each volume: 0.23 dm^{-3}) and a pair of Ag/AgCl electrodes. To ignore the change in the electrolyte's activity coefficient, dilute electrolyte solutions were used. The apparent transport number (\bar{t}_a) was calculated by a following equation [27,28]:

$$E_m = \frac{RT}{F} (1 - 2\bar{t}_a) \ln \frac{C_1}{C_2}, \quad (2)$$

where E_m is the cell potential, R the molar gas constant, T the absolute temperature, F the Faraday constant, and C_1 and C_2 are electrolyte concentrations in low (1 mmol dm^{-3} of NaCl) and high (5 mmol dm^{-3} of NaCl) concentration compartments, respectively.

Current-voltage (I - V) curves were obtained using the two-compartment cell with a $0.025 \text{ mol dm}^{-3}$ NaCl solution for both compartments [27,28]. For the measurement, a pair of Ag/AgCl reference electrodes was positioned at both membrane surfaces and the transport number measurement. The voltage was swept

from 0 to 4.2 V at a scan rate of 10 mV s^{-1} . In addition, chronopotentiometry was carried out 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 transition time to calculate the conductive fraction on the surface of the membranes.

2.3. Diffusion dialysis tests

Dialysis coefficients of the membranes (apparent area: 4 cm by 4 cm) were evaluated using a two-compartment cell initially filled with a feed solution (0.05 mol dm^{-3} FeCl_3 in 2 mol dm^{-3} H_2SO_4) and a permeate solution (deionized water). During the diffusion dialysis experiments, both the compartments were continuously stirred to minimize a concentration polarization effect. Sampling of the permeate solution was performed by every 2 h to measure both acid and iron concentrations. The concentrations of proton and Fe^{3+} ions were determined by an acid-base titration and using a spectrophotometer (DR/4000, HACH, USA) with a FerroVer[®] Iron reagent, respectively. All experiments were performed at room temperature.

3. Results and discussion

3.1. Membrane modification

A series of the Ppy-modified AEMs were prepared by simple spin-coating followed by a dipping process for an interfacial polymerization using a commercial Neosepta-AFX membrane as the substrate. The pictures of the pristine and surface-modified membranes are exhibited in Fig. 1, showing a blue-black color by introducing the Ppy layer on the membrane surface, darkened with increasing the content of Py monomer absorbed in the membrane. In addition, the FE-SEM images show the morphological difference in the surfaces of the pristine, 5 vol.% Py-coated, and 10 vol.% Py-coated membranes, exhibiting the growth of the Ppy domains on the membrane surface in Fig. 2.

3.2. Electrochemical properties of membranes

Since the membranes are electrically charged, the evaluation of their electrochemical properties is of importance to investigate the effect of the Ppy layer on the pristine membrane. In this sense, therefore, various electrochemical analyses, i.e., *a.c.* impedance (for electrical resistance of membranes), linear-sweep voltammetry (for I - V curve), and chronopotentiometry measurements (for the fraction of conducting phase in the surface of membranes) were conducted. The MERs of the membranes are displayed in Fig. 3. The MERs of the Ppy-modified membranes are shown to be slightly higher than that of the pristine membrane, demonstrating that the introduction of the dense Ppy layer on the membrane surface could restrict the ion transport (Cl^- and/or Na^+) owing to both the increased compactness and reduced charge intensity. As a result, it was expected that the crossover of metal ions can be effectively controlled by the introduction of the dense Ppy layer on the membrane surface.

The anion transport numbers (\bar{t}_a) of the membranes are listed in Table 1. The \bar{t}_a values of the Ppy-modified AEMs were shown to be slightly diminished but there are no significant differences compared with that of the pristine AFX membrane. Overall, the Ppy-modified AEMs are shown to have reasonable electrochemical properties comparable to those of commercial membrane.

Fig. 4 shows the I - V characteristics of the pristine and surface-modified AEMs. All the curves exhibit the typical three characteristic regions (i.e., the first region of approximately Ohmic behavior, the second region showing a plateau, and the third region of a

Download English Version:

<https://daneshyari.com/en/article/607425>

Download Persian Version:

<https://daneshyari.com/article/607425>

[Daneshyari.com](https://daneshyari.com)