Reactive and Functional Polymers 132 (2018) 36–42

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Anion-exchange membrane for membrane capacitive deionization prepared via pore-filling polymerization in a porous polyethylene supporting membrane

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ARTICLE INFO

Keywords:
Anion-exchange membrane
Pore-filling polymerization
Porous polyethylene
IEC
Electrical resistance
MCDI

ABSTRACT

Most polymer membranes with a high ion-exchange capacity (IEC) are not dimensionally stable in water because of their excess water uptake. In this study, an anion-exchange membrane was synthesized by performing a pore-filling polymerization in a porous polyethylene membrane used as the supporting substrate. The membrane was found to exhibit a high IEC (3.0 meq/g) but a very low water uptake (8%) and low electrical resistance (0.30 Ω·cm^2). The membrane capacitive deionization (MCDI) cell assembled from components including the fabricated anion-exchange membrane and a commercial cation-exchange membrane (CMX) was found to exhibit a higher salt adsorption capacity and a higher current efficiency than that using a commercial anion-exchange membrane (AMX, IEC = 1.5 meq/g, electrical resistance = 4.8 Ω·cm^2) and CMX. This improved performance compared to that of the AMX cell is ascribed to the higher IEC of the new membrane and its lower electrical resistance.

1. Introduction

Desalinated water makes up a major proportion of potable water, and is critical to sustaining life and economic growth. In recent years, many water desalination systems have been developed based on electro-separation techniques, such as electro-dialysis (ED), electro-deionization (EDI), and capacitive deionization (CDI), which produce fresh water from saline or brackish water. In the past decade, there has been remarkable progress in CDI systems, which have been studied from various perspectives such as their theoretical and architectural aspects as well as their materials and performance [1–4].

In a CDI system, undesirable minerals and salts are removed from water samples by passing them through electrically charged electrodes. These electrodes attract oppositely charged ions, and the charged ions are adsorbed onto the surfaces of the porous electrodes (usually carbon). Finally, deionized or demineralized water is generated as a product [5–7]. CDI is a cost-effective, clean and green technology [3]. However, there are some issues that limit the efficiency of such systems, including the oxidation of the anode electrode and charge leakage in the electric double layer due to the adsorption of co-ions [8–10]. To overcome these problems, membrane capacitive deionization (MCDI) was introduced [11,12]. In MCDI cells, ion-exchange membranes are placed between each carbon electrode and a spacer (a water channel), which results in the expulsion of co-ions and leads to an increased flux of counter ions to neutralize the co-ions. In addition, the membranes prevent the adsorption of co-ions onto the opposite electrode during the reverse-potential-induced desorption process, which results in the efficient removal of ions from the feed solution [13,14].

The commercial ion-exchange membranes produced by Astom, Filmtech, and Fujifilm for ED and EDI systems have also been used in MCDI systems. Despite their great success, there are still many constraints on their use, such as high prices (approximately $100–200/m^2) and low ion-exchange values (< 2.0 meq/g). In addition, commercial membranes are usually very thick (> 50 μm) and have high electrical resistances (> 3 Ω·cm^2), which limits their salt adsorption capacities in MCDI operation. They also have low durability due to their direct contact with the feed water flow, which has a high level of salinity and thus can lead to wear and tear after a certain period of time [15,16]. Therefore, extensive studies are required to produce ion-exchange membranes that are suitable for MCDI.

Overall, ion-exchange membranes for MCDI applications should have high IEC values, low electrical resistance, high mechanical strength, and high dimensional stability. One possible method for the preparation of ideal ion-exchange membranes is the use of a supporting

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https://doi.org/10.1016/j.reactfunctpolym.2018.09.010
Received 11 May 2018; Received in revised form 31 August 2018; Accepted 10 September 2018
Available online 13 September 2018
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membrane. The supporting membrane can be filled with ion-exchangeable monomers, followed by polymerization (pore-filling polymerization). Alternatively, the supporting membrane is filled with monomers, followed by polymerization and functionalization in order to incorporate ion-exchangeable groups into the resulting polymer chains. Various cation-exchange membranes have been prepared by using polymer supporting membranes such as polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), and polyethylene (PE) [17–22]. However, no study of pore-filled anion-exchange membranes for MCDI has been reported to our knowledge, even though anion-exchange membranes are also important in their own right.

In this study, an anion-exchange polymer-filled PE membrane (AEP-PEM) was synthesized via the pore-filling polymerization method. Crosslinked poly(chloromethylstyrene) was prepared in a highly porous low-density PE membrane (PEM) via the pore-filling polymerization of chloromethylstyrene and divinylbenzene (the crosslinking agent). The pore-filled poly(chloromethylstyrene) in the PEM was functionalized to contain anion-exchange functional groups. The chemical structures and thermal properties of the membrane were characterized by using FT-IR spectroscopy, elemental analysis, and thermogravimetric analysis. The membrane's IEC, water uptake, dimension stability, and electrical resistance were also measured. MCDI cells were assembled from components including the synthesized anion-exchange membrane and a commercial cation-exchange membrane (CMX), and their performances, such as their salt removal capacities, salt removal efficiencies, and charge efficiencies, were determined.

2. Experimental

2.1. Materials

Microporous PEM (thickness: 25 μm, porosity: 45%, pore size: 70 nm) was purchased from Asahi Chemicals, Japan. 4-(Chloromethyl) styrene (CMS), divinylbenzene (DVB) and 1-methylimidazole were purchased from Sigma Aldrich Chemical Co. Benzoyl peroxide (BPO) and aqueous phenolphthalein (1%) were purchased from Dae-Jung Chemicals & Metals Co. and Junsei Chemical Co., respectively.

Acetonitrile, 0.5 N sodium hydroxide solution, 0.5 N hydrochloric acid solution, toluene, and acetone were purchased from Samchun Pure Chemical Co. All these chemical reagents and solvents were used as received. A cation-exchange membrane, CMX (Neosepta, thickness: 170 μm) and an anion-exchange membrane, AMX (Neosepta, thickness: 140 μm) were purchased from Astom Corporation, Japan. A graphite sheet (F02511, thickness: 250 μm) was purchased from Dongbang Carbon Co., Korea. Carbon electrodes were prepared from activated carbon powder (CEP-21 K, Power Carbon Technology Co., Korea), carboxymethyl cellulose (CMC, dispersing agent), and styrene butadiene rubber (EQ-Lib-SBR, MTI Co. polymer binder) in a weight ratio of 9:0.1:1 [23].

2.2. Synthesis of the pore-filled ion exchange membrane

A pore-filled membrane was fabricated by introducing a monomer solution into the pores of a PEM sample. Square pieces of PEM (10 cm × 10 cm) were soaked in acetone for 1 h, dried and weighed. The monomer solution was prepared by mixing 5% DVB in 10 mL of CMS (monomer) containing BPO (the radical initiator). The porous PEM was immersed in the monomer solution for 10 min at room temperature for complete impregnation of the reactants into its pores. After monomer sorption, the wet membrane was sandwiched between poly (ethylene terephthalate) films supported by glass plates. After radical polymerization at 80 °C for 12 h in an oven, the membrane was washed with toluene to remove excess compounds from its surface and then washed with deionized water.

2.3. Surface chemical modification – Functionalization

The PEM filled with poly(chloromethylstyrene) (PCMS-PEM) was functionalized by soaking it in a mixture consisting of 50 mL methanol, 50 mL acetonitrile, and 4.0 mL 1-methylimidazole for 24 h at 70 °C. Finally, the resulting membrane (AEP-PEM) was washed with acetone and deionized water, then wiped, followed by drying and storage at room temperature.

2.4. Instrumental analyses of AEP-PEM

The functional groups of the membrane were confirmed by performing Fourier-transform infrared (FT-IR) spectroscopy (JASCO 4100E FTIR spectrometer) under ambient conditions over the wavenumber range 4000–600 cm^{-1}. Surface and cross-section images of the prepared membrane were recorded with field emission scanning electron microscopy (FESEM, Hitachi SU-70). The thermal stabilities of all the membranes were investigated by using thermogravimetric analysis (TGA, SDT Q600) at a heating rate of 10 °C/min in the range 25–800 °C under a nitrogen atmosphere. The contact angles of water on the membranes were determined at room temperature by using a contact angle measuring meter (Surface Electro Optics Phoenix 150). The contact angle for each sample was measured five times and the average value is reported here.

2.5. Ion-exchange capacity (IEC)

The ion-exchange capacities (IECs) of the membranes were determined with the standard titration method [17]. The anion-exchange membrane was soaked in 0.5 M NaOH standard solution, sonicated for 30 min and left to stand for 24 h at 25 °C for complete substitution of ions. Subsequently, after the membrane was removed from solution, the residual solution was titrated against a 0.5 M aqueous standard solution of HCl with phenolphthalein as the indicator. The IECs of AMX and CMX were also measured by above method. The IEC value was reported as the average of four specimens. The IEC value of a sample can be calculated with the following equation:

$$\text{IEC (meq/g)} = [C_T \times V_T]/W_{dry}$$

where C_T is the concentration of the titrant solution, V_T is the volume of the titrant solution, and W_{dry} is the weight of the membrane sample.

2.6. Dimensional stabilities and water uptakes

The membranes were dried in an oven at 80 °C for 24 h, then immersed in deionized water at 25 °C for 24 h.

The membranes were removed from the water, wiped with tissue paper, then characterized. Their water uptakes and swelling ratios were calculated by using the following equations:

$$\Delta L(\%) = [L_{wet} - L_{dry}]/L_{dry} \times 100$$

$$\text{Water uptake } (\%) = [W_{wet} - W_{dry}]/W_{dry} \times 100$$

where L_{wet} and L_{dry} are the lengths of the wet and dry membranes respectively, and W_{wet} and W_{dry} are the weights of the wet and dry membranes respectively.

2.7. Electrical resistances

The electrical resistances of the membranes were measured by using a clip cell and an LCRZ meter (DU-6011, Delta Inc.). Prior to the measurements, the samples were pre-equilibrated in a 2.0 M NaCl standard solution for 24 h, and placed between a two-compartment cell where each chamber is equipped with a 1 cm^2 platinum electrode. The resistance of each sample was measured by impedance spectroscopy using LCR meter in the frequency of 1 kHz. Each cell was filled with a

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