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Preparation of polyethylene membranes filled with crosslinked sulfonated polystyrene for cation exchange and transport in membrane capacitive deionization process

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ABSTRACT

Commercial ion-exchange membranes are usually thick, and have high electrical resistances that can reduce the adsorption capacity of electrodes in membrane capacitive deionization (MCDI) cells. In this study, porous polyethylene (PE) membranes, filled with a sulfonated monomer, crosslinking agent (5, 10, 15 wt%), and radical initiator, were subjected to polymerization and subsequent ion-exchange, to yield PE filled with crosslinked sulfonated polystyrene (PE-CSPS-5, 10, 15). PE-CSPS membranes were very thin (27 μm), and exhibited moderate water uptake (26–35 wt%) and ion-exchange capacity (0.70–1.0 meq/g), and low electrical resistances (0.33–0.62 Ω·cm^2) compared with commercial ones. MCDI cells were assembled with either a PE-CSPS-5 membrane or a commercial cation-exchange membrane (CMX, IEC 1.5–1.8 meq/g), and their performances studied using a 500 ppm solution of NaCl. The current efficiency of the PE-CSPS-5-based MCDI cell showed slightly higher than that of the commercial CMX-based MCDI cell, which was attributed to the considerably lower electrical resistance of the membrane (0.33 *vs.* 2.9 Ω·cm^2), even though its IEC value is smaller (1.0 *vs.* 1.5–1.8 meq/g). Our study reveals that supporting membranes filled with ion-exchange polymers have advantages over casting membranes in preparing membranes for MCDI application, with respect to dimentional stability and thickness.

1. Introduction

Water is one of the most important and fundamental natural resources used by mankind, but sources are becoming threatened due to increasing populations, industrial development, and environmental pollution. It is thus necessary to develop novel technologies to enable the production of fresh water from sea or brackish water [1–2]. Capacitive deionization (CDI) is a technology used for water treatment and desalination, in which minerals and salts are removed from a solution by passing it through an electric field between two electrodes [3–6]. Ions can be simply adsorbed or desorbed by changing the potential of the electrodes. The process produces no contaminants during regeneration of electrodes, and is environmentally friendly. Therefore, CDI is a cost-effective and environmentally-friendly deionization technology [7–10].

In CDI cells, carbon electrodes with high specific surface areas are commonly employed for efficient adsorption of ions. When a potential is applied to the cell, counterions are adsorbed in the electrical double layer, while co-ions are expelled from pores inside the carbon electrode. The co-ions migrate to the spacer channel, resulting in a decrease in desalination efficiency [11–13]. To overcome this problem, membrane capacitive deionization (MCDI) has been introduced [14–17]. In MCDI cells, a cation-exchange membrane is placed between a carbon electrode (cathode) and a spacer, and an anion-exchange membrane is placed between the same spacer and the opposite electrode (anode). With this cell configuration, ions are removed from the aqueous solution flowing through the spacer and adsorbed on the surfaces of the electrodes, resulting in an effluent with a reduced ion concentration [18]. When applying 0.0 V or a reversed voltage for desorption, ions adsorbed on the surface of the electrodes can be released back into the aqueous solution to generate a product stream with a high ion concentration [18,19]. For example, cations released back from the

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cathode can pass through the cation-exchange membrane and reach the spacer. However, they cannot pass through the anion-exchange membrane to adsorb onto the anode due to the repulsion of anion-exchange membrane, which thus leads to an improvement in salt removal efficiency.

A considerable amount of research has been conducted on MCDI systems. For example, Lee et al. reported a MCDI system with a salt removal rate 19% higher than that of a CDI system [20]. Li et al. constructed MCDI devices using carbon nanotubes and nanofiber electrodes and found that the salt removal efficiency of the system was about 50% higher than that of a CDI system [21]. Kim and Choi also reported that the salt removal efficiency of the MCDI cell was enhanced by 33–56% compared to the CDI cell [16]. They also reported that when the MCDI cells were assembled with carbon electrodes coated with a cation-exchange polymer, poly(vinyl alcohol) crosslinked with sulfosuccinic acid, the salt removal efficiency and current efficiency of the cells were enhanced by 27–56% and 69–95%, respectively, compared to the CDI cell.

Ion-exchange membranes are very important constituents of MCDI cells [22]. Commercial ion-exchange membranes are usually very thick for enough mechanical strength [23]. However, such thick membranes have high electrical resistances that can reduce the adsorption capacity of electrodes at a given voltage. To improve dimensional stability, it would be possible to use a supporting membrane that would limit swelling of the filled ion-exchange polymer to below a particular extent. Simons et al. reported a new type of anion-exchange membranes, *via* irradiation of microporous films in a grafting solution containing 4-vinylpyridine with γ-rays, followed by quaterization using methyl iodide or methyl sulfate [24]. Childs and co-workers reported pore-filled membranes, composed of a microporous substrate (polyethylene or polypropylene) and a pore-filling crosslinked polyelectrolyte hydrogel [25,26]. The supporting membrane can be filled with ion-exchangeable monomers, followed by polymerization. Alternatively, monomers filling the supporting membrane can be polymerized and subsequently functionalized to incorporate ion-exchangeable groups to the filled polymer chains. Various ion-exchange membranes have been prepared from different types of polymer supporting membranes, such as polyethylene, poly(tetrafluoroethylene), polycarbonate, polypropylene, poly(vinylidene fluoride) [27-30]. However, to our best knowledge, such membrane-based MCDI cells have not yet been reported in literature.

PE membranes with crosslinked sulfonated polystyrene were already published in the literature [31], but our synthetic method is quite different from the reported one, with respect to monomer type and sulfonation. Briefly, the previous membranes were prepared by three steps: pore-filling with monomers, polymerization and sulfonation under strongly acidic conditions. In this study therefore, commercial low density polyethylene films were filled with a solution of tertrabutylammonium 4-vinylbenzenesulfonate (TVS), divinylbenzene and 2,2-azobis(2-methylpropionitrile), followed by polymerization. The resulting membranes were then treated with 1.0 N HCl solution to exchange tetrabutylammonium ions with protons and ultimately obtain PE membranes filled with crosslinked sulfonated polystyrene (PE-CSPS). Our current synthetic method has an advantage over the previous one, because our method easily controls the degree of sulfonation and avoids of using the highly acidic condition for sulfonation [27].

The chemical structure and morphology of the PE-CSPS membranes were confirmed by Fourier-transform infrared (FT-IR) spectroscopy and scanning electron microscopy, respectively. Thermal stability of the membranes was measured, together with ion-exchange capacity, water uptake, dimensional stability, and electrical resistance. Finally, MCDI cells were assembled using the PS-CSPS membranes, and their performances investigated using a 500 ppm solution of NaCl.

2. Experimental

2.1. Material

Microporous polyethylene (PE) was purchased from Asahi chemicals (thickness 25 μm, average porosity 45%, and mean pore size 70 nm). Sodium 4-divinylbenzene sulfonate was purchased from Sigma Aldrich Chemical Co. Hydrochloric acid (35–37%), 1.0 N hydrochloric acid solution, magnesium sulfate, sodium chloride, sodium hydroxide, methylene chloride, and acetone were purchased from Samchun. Azobisisobutyronitrile (AIBN, 99%) and tetrabutylammonium bromide were purchased from DAEJUNG. Divinylbenzene (DVB) was obtained from TCI. All chemicals were used as received without further purification. A cation-exchange membrane (CMX, thickness 170 μm, IEC 1.5 meq/g) and an anion-exchange membrane (AMX, thickness 140 μm, IEC 1.4 meq/g) were purchased from Astom Co., Japan. A graphite sheet (F02511) was purchased from Dongbang Co., Korea. TVS was prepared from sodium 4-vinylbenzenesulfonate and tetrabutylammonium bromide by the procedure developed in our laboratory [27]. Carbon electrodes were prepared by mixing activated carbon powder, polymer binder, and a dispersing agent, as previously reported in literature [28].

2.2. Preparation of PE-CSPS

PE films were immersed in a solution of TVS, DVB, and AIBN (0.5 wt% with respect to total weight of TVS and DVB) for longer than 5 min. Three different weight ratios of TVS to DVB were employed: 95/5, 90/10, and 85/15. After immersion, the PE films were sandwiched between poly(ethylene terephthalate) films and polymerized at 70 °C for 10 h in an oven, then washed with methylene chloride to remove any unreacted compounds. The membranes were then immersed in 1.0 N HCl solution for 24 h and washed with deionized water. This ion-exchange procedure was repeated several times, and the membranes were then dried in a vacuum oven. The resulting membranes were designated PE-CSPS-5, PE-CSPS-10, and PE-CSPS-15, respectively, where the numbers indicate the percent of DVB with respect to the total feed weight of TVS and DVB employed.

2.3. Chemical structure and morphology analysis

FT-IR spectra were recorded on a JASCO 4100E FT-IR spectrometer under ambient conditions over a wavenumber range of 4000–600 cm^{-1}. Surface and cross-sectional images of PE membranes were obtained on a field emission scanning electron microscope (FE-SEM, HitachiSU-70).

2.4. Water uptake and dimensional stability

The membranes were dried at 100 °C for one day and then immersed in deionized water at 25 °C for another day. The change in length and water uptake of the membranes were calculated from 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, and W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

2.5. Ion-exchange capacity (IEC)

The membranes were immersed in 1.0 M NaCl solution for 24 h at room temperature, then removed, and the resulting solutions were titrated using 0.01 N NaOH solution. The IEC value was calculated from