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# Nanofibrous composite membranes (NFCMs) for mono/divalent cations separation

Linxiao Hou, Jiefeng Pan, Dongbo Yu, Bin Wu, Abhishek N. Mondal, Qiuhua Li, Liang Ge*, Tongwen Xu*

*CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China*

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ABSTRACT

The development of cation-exchange membrane with the ability to effectively separate mono/divalent ions is of crucial importance to various industrial applications such as wastewater purification and seawater desalination. However, it remains a big challenge to fabricate monovalent cation selective membrane maintaining both of high ion flux and good permselectivity. In this study, nanofibrous composite membranes (NFCMs) containing $-N^{+}(CH_3)_3$ and $-SO_3^{-}$ groups are fabricated by impregnating bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) electrospun nanofibrous mats into sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) solution and followed by quaternization of the bromomethyl groups. The unique nanofibrous composite structure results in low electrical resistance, high limiting current density ($i_{lim}$) and significant improvement in dimensional stability and ion flux. In addition, due to the introduced quaternized electrospun nanofibrous mats, monovalent cations can be separated from divalent cations by their difference of electrostatic repulsion force. Compared with the commercial monovalent cation selective membrane (CSO), the optimized membrane (NQS1) in this study shows better performance with the ion flux of $2.96\times10^{-8}$ mol cm$^{-2}$ s$^{-1}$ and the permselectivity of 1.62 in an electrodialysis process (feed solution: 0.1 mol L$^{-1}$ NaCl /$MgCl_2$). According to the excellent performances, our nanofibrous composite membranes are expected to be a promising candidate for $Na^{+}/Mg^{2+}$ separation.

## 1. Introduction

Water crisis such as freshwater exhaustion and wastewater pollution is a worldwide problem. Electrodialysis (ED) which employs electrically charged ion exchange membranes with an electrical potential difference as driving force for ion separation has been proven as an emerging technology to solve these problems [1–4]. The related electrodialysis applications can be found in various fields such as waste acid recovery, brine reclamation [5,6], and bio-fermentation engineering [7]. However, the sedimentation of multivalence cations hydroxide always leads to the formation of fouling on membrane surface which limits the ED industrial applications. Bruggen et al. reported that electrodialysis with monovalent selective membrane could be an efficient approach to overcome this issue [8]. Although the representative monovalent cation selective membranes such as CSO (Selemion, Japan) and CMS (Neosepta, Japan) have been widely used in practical applications [9], the price and separation performance remain unsatisfying. Therefore, it is urgent to develop inexpensive monovalent cation selective membranes with high flux and permeability. Meanwhile, some other important properties including thermal and chemical stability, high limiting current density and low resistance should be also taken into account [10].

Several aspects like the affinity between ions and functional groups, ion mobility and operation conditions synergistically determine the membrane permselectivity [11]. Therefore, these factors should be appropriately considered during membrane modification. The general mechanisms for mono/divalent separation can be divided into two classification, one is pore-size sieving effect and the other is electrostatic repulsive force interaction [3]. To date, a plenty of approaches have been explored to enhance the mono/divalent cations separation efficiency. For example, based on pore-size effect, fabricating extraordinary dense membranes by chemical crosslinking [12], tuning crystallinity [13] and constructing acid-base pairs ion channels have been reported to be effective. However, the rigid structure would inevitably increase the electrical resistance and reduce the ion flux [14], therefore, a promising approach has been proposed in which the

* Corresponding authors.
*E-mail addresses:* geliang@ustc.edu.cn (L. Ge), twxu@ustc.edu.cn (T. Xu).

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**Nomenclature**

| | |
|---|---|
| NFCM | nanofibrous composite membrane |
| ED | electrodialysis |
| IEM | ion exchange membrane |
| LBL | layer-by-layer |
| SEM | scanning electron microscope |
| ATR-FTIR | attenuated total reflectance Fourier transform infrared |
| TGA | thermogravimetric analysis |
| DTG | derivative thermogravimetry analysis |
| WU | water uptake |
| SD | swelling degree |
| I-V curves | current-voltage curves |
| ICP-AES | inductively coupling plasma-atomic emission spectrometer |
| QPPO | quaternized poly(2,6-dimethyl-1,4-phenylene oxide) |
| SPPO | sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) |
| BPPO | bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) |
| PPO | poly (2,6-dimethyl-1,4-phenylene oxide) |
| NMP | N-methyl-2-pyrrolidone |
| TMA | trimethylamine |
| rpm | rotation per minute |
| J | ion flux (mol $cm^{-2}$ $s^{-1}$) |
| P | permselectivity |
| $C_t$ | ion concentration after electrodialysis (mol $cm^{-3}$) |
| $C_o$ | initial ion concentration (mol $cm^{-3}$) |
| V | volume of concentrated chamber ($cm^3$) |
| $A_m$ | effective area of membrane ($cm^2$) |
| $W_d$ | weight of dehydrated membrane (g) |
| $W_w$ | weight of hydrated membrane (g) |
| $A_d$ | area of dehydrated membrane ($cm^2$) |
| $A_w$ | area of hydrated membrane ($cm^2$) |
| $E_m$ | membrane potential (V) |
| $t_i$ | transport number of counter-ions in membrane |
| R | gas constant ($JK^{-1}mol^{-1}$) |
| T | absolute temperature (K) |
| F | Faraday constant ($Cmol^{-1}$) |
| z | electrovalence |
| $a_{1\&}$ $a_2$ | mean activities of the electrolytes |
| $R_{or}$ | resistance in ohmic region (Ω $cm^2$) |
| ΔE | plateau length (V) |

membrane surface is modified with a thin and positively charged layer. According to Coulomb's law, the electrostatic repulsive force confronted by monovalent and divalent cations in fixed positively charge systems matches the order of 1:2, which can generate selectivity for mono/divalent cations separation. Some reported monovalent cation selective membranes with cationic polyelectrolytes (such as polyethyleneimine [15,16], polyquaternium-7 [17], polyaniline [18] or polypyrrole [19]) have been investigated in previous works, but the permselectivity of these membranes is still not good enough to enable an efficient separation of $Na^+/Mg^{2+}$. The layer-by-layer (LBL) assembly of polyelectrolyte multilayers is found to be a good alternative [20]. In this method, alternating adsorption of polycations and polyanions on Nafion membrane leads to extremely high mono/divalent cations permselectivity ($K^+/Mg^{2+}$ permselectivity > 1000) [21]. Nevertheless, when the current exceeds a limiting current density of 2.54 mA $cm^{-2}$, it shows highly decreasing permselectivity. More importantly, it is very difficult to realize its large-scale applications because of the extremely low limiting current density and complex fabrication process.

In order to repel the divalent ions throughout the membrane rather than only on the surface, herein we prepare nanofibrous composite membranes with a characteristic mosaic structure, by embedding positively charged electrospun nanofibrous mats in a negatively charged polymer matrix. The cationic nanofibers are fabricated by a facile and efficient electrospinning method which play a key role of the final charge-guided ion separation; meanwhile, the negatively charged SPPO as the membrane matrix can facilitate the ion transportation; as a result, the continuous selective separation and the fluent transport channel endow the nanofibrous composite membranes with high ion flux and permselectivity. The analytical techniques such as scanning electron microscope (SEM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) and elemental analysis are used to characterize the composition and morphology of the membranes. In addition, thermogravimetric analysis (TGA)/ derivative thermogravimetry analysis (DTG), water uptake (WU), swelling degree (SD), current-voltage (I-V) curves and transport numbers are also measured to investigate the physicochemical and electrochemical properties. The separation performance of membranes are evaluated through electrodialysis experiments in binary systems ($Na^+/Mg^{2+}$). For the optimized membrane NQS1, the obtained permselectivity and ion flux are superior to those of the commercial CSO membrane. Our study has demonstrated that the nanofibrous composite membranes constructed by electrospinning can be a good candidate for electro-driven separation of ions.

## 2. Experimental

### 2.1. Materials

Commercial membranes used during ED test were Neosepta AMX (anion-exchange membrane, Tokuyama Co., Japan) and CSO (Selemion, Japan). The electrospinning device was bought from Beijing Yongkang Leye Technology Development Co Ltd. (Beijing, China). Sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO) in $Na^+$ form (IEC ≈2.1 mmol $g^{-1}$), and Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) was supplied by Tianwei Membrane Co. Ltd. (Shandong, China). Bromomethylated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) with 75% of methyl bromination was synthesized according to a previously reported literature [22]. Methanol, N-methyl-2-pyrrolidone (NMP), trimethylamine (TMA) aqueous solution (33.3 wt%), NaCl, $MgCl_2$, $Na_2SO_4$ were used as received.

### 2.2. Preparation of BPPO electrospun nanofibrous mat

BPPO electrospun nanofibrous mat was fabricated by electrospinning BPPO solution. In a typical procedure, a 25% w/w clear homogeneous solution was firstly prepared by dissolving BPPO into NMP solvent. Subsequently, proper amount of BPPO solution was electrospun at 19 kV with a flow rate of 0.07 mL $min^{-1}$ at a relative humidity of 30% under 30 °C, and the electrospun BPPO nanofibers were collected on the aluminum foil covering a cylindrical counter electrode (rotated at 200 rpm and horizontally oscillated at 150 rpm). After electrospinning for 14 h, BPPO electrospun nanofibrous mat with enough mechanical properties was obtained. In order to remove the residual NMP and slightly crosslink BPPO fibers, the mat was put into vacuum oven at 90 °C for 3 h [23], following with pressing treatment under 5 MPa for 30 min after cautiously peeling it off from the aluminum foil.

### 2.3. Fabrication of nanofibrous composite membranes

A 25 wt% of SPPO solution was prepared in methanol at room temperature under continuous stirring. The electrospun nanofibrous mat prepared above was cut into rectangles (5 cm×6 cm) and fixed by normal scotch type on a clean glass plate. Then the SPPO solution was