



Preparation of a monovalent selective anion exchange membrane through constructing a covalently crosslinked interface by electro-deposition of polyethyleneimine



Jiefeng Pan^{a,1}, Jincheng Ding^{a,1}, Ruiqing Tan^a, Guangyao Chen^a, Yan Zhao^a, Congjie Gao^a, Bart. Van der Bruggen^{b,c}, Jiangnan Shen^{a,*}

^a Center for Membrane Separation and Water Science & Technology, Ocean College, Zhejiang University of Technology, Hangzhou 310014, PR China

^b Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200 F, B-3001 Leuven, Belgium

^c Faculty of Engineering and the Built Environment, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa

ARTICLE INFO

Keywords:

Monovalent selective anion membranes
Polyethyleneimine (PEI)
Electrodialysis
Covalent immobilization
Electro-deposition

ABSTRACT

Surface modification by generating a dense anionic layer on the surface of a substrate membrane is the main method for preparing monovalent selective anion exchange membranes. However, this method has a trade-off between the permselectivity and the stability of the surface layer. To overcome this problem, a simple preparative pathway is devised to covalently immobilize the polyethyleneimine (PEI) onto the surface of an anion exchange membrane (partly quaternized poly (phenylene oxide) (QPPO)). Firstly, a brominated poly (2,6-dimethyl-1, 4-phenylene oxide) (BPPO) based anion membrane was prepared by quaternization. Then, this membrane was modified by electro-deposition of a PEI solution. The composition and structure of the membrane were observed by infrared spectroscopy and scanning electron microscopy. The permselectivity was evaluated by electrodialysis in a Cl⁻/SO₄²⁻ system. The experimental results prove that the PEI modification method is an effective, simple, feasible and well-controlled strategy to fabricate mono-valent selective anion membranes.

1. Introduction

Electrodialysis (ED), an electro-membrane-separation process utilizing the electric potential difference as the driving force, is applied for desalination of brackish water, and also in the purification and the treatment of effluents, wastewater, and waste gases [1–4]. However, the complexity of raw water poses a great challenge to the ion exchange membrane technology. Examples include the removal of F⁻ or NO₃⁻ from groundwater and the separation of SO₄²⁻ for avoiding scale formation in water treatment processes [5–10]. In these processes, the separation of mono/multi-valence ions plays a critical role. Compared to other ion separation technologies like nanofiltration, chemical precipitation, and adsorption, the electrodialysis process based on monovalent selective anion membranes allows for recycling of toxic waste fractions [11]. As the core component of an ED device, the monovalent selective anion exchange membrane can selectively transport monovalent anions but rejects (nearly) all multivalent anions. Nevertheless, due to the lack of high performance monovalent selective anion exchange membranes, ED has been rarely reported for the treatment of high fluoride or

nitrate-containing effluents [12,13]. To achieve an excellent separation performance, considerable research efforts have been devoted to the exploration of monovalent selective anion exchange membranes with high permeability for monovalent anions (i.e., Cl⁻ or F⁻) as well as a high rejection of multivalent anions (i.e., SO₄²⁻). The theoretical foundation of the methods is mainly based on the different properties of ions, such as (hydrated) ionic radius, valence (electrostatic repulsion) and dehydration energy of hydrated ions [14].

Considering the difference in properties of mono/multivalent anions, many strategies have been explored for preparing monovalent selective anion exchange membranes, mainly based on the sieving mechanism and electrostatic repulsion mechanism [15]. One of the most promising strategies is to densely deposit a negatively or positively charged layer onto the surface of a common anion exchange membrane (AEM) [16,18,31]. For example, Shahi [16] and co-workers found that an AEM coated by a thin polypyrrole layer would increase the membrane permselectivity from 0.747 to 0.889. Matsuyama's research group [17] reported a chloride selective membrane by the alternating layer-by-layer deposition of poly-cations and poly-anions. It

* Corresponding author.

E-mail address: shenjn@zjut.edu.cn (J. Shen).

¹ Contribute equally to the manuscript.

Nomenclature	
PEI	Polyethyleneimine
QPPO	Partly quaternized poly (phenylene oxide)
BPPO	Brominated poly (2,6-dimethyl-1, 4-phenylene oxide)
ED	Electrodialysis
AEM	Anion exchange membrane
CEM	Cation exchange membrane
NMP	1-methyl-2-pyrrolidone
TMA	Trimethylamine
A ₀	The based materials BPPO
A ₁	BPPO based anion exchange membrane
EA ₁	Single surface modified anion exchange membrane
EA ₂	Double surfaces modified anion exchange membrane
ATR-FTIR	Attenuated Total Reflectance - Fourier transform Infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
SEM	Scanning electron microscope
IEC	Ion exchange capacity
R _n	Resistance of the membrane expressed in Ω cm ²
U	Voltage of the membrane in V
U ₀	The voltage value of blank in V
S	The membrane effective area cm ²
PEI-QPPO	Partly quaternized poly (phenylene oxide) is modified by polyethyleneimine
$P_{SO_4^{2-}}^{Cl^-}$	Permselectivity of Cl ⁻ against SO ₄ ²⁻

was found that the monovalent anion selectivity increased with increasing numbers of deposited layers (SO₄²⁻/Cl⁻ selectivity = 0.4 after 15 layers modified). Afterwards, Shen et al. [19] reported a monovalent selective anion exchange membrane modified by the same alternate electro-deposition method. The monovalent anion selectivity increased to 2.9 and the separation efficiency increased to 0.28 when nine bilayers were introduced. However, in these studies, the surface layers are attached on the support membrane by hydrogen bonds or Van der Waals forces, and the long term stability (detachment between the active layer and matrix) attracts controversy despite their relatively good permselectivity.

In order to overcome these problems, the attention has shifted to developing a stronger binding force between the active layer and the substrate membrane. For example, Matsuyama et al. [9] prepared a modified AEM with single layer poly-dopamine and achieved an excellent selectivity for monovalent anions ($P_{SO_4^{2-}}^{Cl^-} = 4.5$). To further improve the binding force between the matrix and the active layer, Wang et al. [10] developed a covalent modification procedure for preparing monovalent selective anion exchange membranes ($P_{SO_4^{2-}}^{Cl^-} = 2.8$), including the introduction of carboxyl groups by a chemical reduction of aryl diazonium salts, PEI immobilization via an amidation reaction followed by deposition of glutaraldehyde-induced PEI multilayers. However, modified membranes based on polydopamine often lack a uniform and long term stable structure, and a reduction of the overall performance seems unavoidable due to the increase in the membrane resistance [20]. A covalent modification procedure, requiring particular equipment or a complex process control, is needed and restricts its further application.

Herein, a simple preparative pathway is devised to covalently immobilize polyethyleneimine (PEI) on the surface of an anion exchange membrane (partly quaternized poly (phenylene oxide) (QPPO)), as shown in Fig. 2. By varying the conditions of electro-deposition, the perm-selectivity and membrane resistance can be easily regulated. The compositions and structures of the membranes were observed by infrared spectroscopy and scanning electron microscopy. The permselectivity was evaluated by electro-dialysis employing a Cl⁻/SO₄²⁻ system.

2. Experimental

2.1. Material

Brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) with aryl substitution degree of 0.42 and benzyl substitution degree of 0.58 was supplied by Tianwei Membrane Co. Ltd., Shandong, China. Commercial anion exchange membrane Neosepta AEM and cation exchange membrane Neosepta CEM were purchased from FUJIFILM Corp., Japan. The characteristic properties of these commercial ion exchange membranes are shown in Table 1. Furthermore, 1-methyl-2-pyrrolidone (NMP, 99.5%), poly(ethyleneimine) solution (PEI, 30 wt%, Mw

750,000), trimethylamine (TMA), Sodium chloride (NaCl) and sodium sulfate (Na₂SO₄) were purchased from Aladdin Reagent Co. Ltd., Shanghai, China, and used without further purification. Distilled water was used throughout. The structures of BPPO and PEI are shown in Fig. 1(a) and (b), respectively.

2.2. Preparation of partly quaternized BPPO-based anion exchange membrane (QPPO)

The partial quaternization reaction of BPPO was conducted according to previous work [21]. BPPO (5 g) was firstly dissolved in NMP to form a homogeneous solution with a concentration of 20% (w/w). Afterwards, 1.5 mL TMA solution was added. After this, the solution was still stirred vigorously for 12 h at 25 °C to ensure the complete reaction between the BPPO and TMA. Finally, the solution was casted onto a clean glass plate with a steel knife and heated at 70 °C for 8 h. Then the obtained anion exchange membrane was peeled off from the glass plate in water. The membrane has a thickness of 45–47 μm; it was washed with distilled water before using. This membrane was named QPPO membrane. The chemical reaction for preparing QPPO is represented in Scheme 1.

2.3. Surface modification of QPPO membrane

The polyethyleneimine solutions were prepared by dissolving polyethyleneimine with a concentration of 10 g L⁻¹ and with 0.5 M NaCl (as a supporting electrolyte) in distilled water. The surface modification process of the QPPO membrane was carried out by using a custom-designed ED stack apparatus with four cells [22]. The QPPO membrane was clamped in the middle of the four cells and the other two auxiliary membranes were both cation exchange membranes; one of the QPPO membrane surfaces was turned to anode, as shown in Fig. 3. The effective membrane surfaces areas are all 19.625 cm² and the solution volume is 400 mL. The polyethyleneimine with 0.5 M NaCl solutions were placed in one compartment of the two middle cells, and a 0.5 M NaCl solution was placed in the other compartment. Solutions of 0.2 M Na₂SO₄ were used as electrode solution for both cathode and anode. Then one surface of the QPPO membrane was modified via an ED experiment with the polyethyleneimine solutions. Alternatively, the other surface was modified through exchanging the solutions of the two middle cells and electrodes of the DC-power supply. The membrane

Table 1
Properties of the commercial CEMs and AEMs used in this study.

Membrane type	Thickness (μm)	Electrical area resistance (Ω cm ²)	pH stability
Homogeneous (AEM)	125	1.3	2–10
Homogeneous (CEM)	135	2.7	4–12

Download English Version:

<https://daneshyari.com/en/article/4988786>

Download Persian Version:

<https://daneshyari.com/article/4988786>

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