



Electric-pulse layer-by-layer assembled of anion exchange membrane with enhanced monovalent selectivity

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ABSTRACT

The present study investigates the electric-pulse layer-by-layer assembled of anion exchange membrane (AEM) by N-O-sulfonic acid benzyl chitosan (NSBC) and hydroxypropyl trimethyl ammonium chloride chitosan (HACC). The constructed NSBC/HACC layers by electric-pulse deposition method with 7.5 bilayers exhibit substantial influence on monovalent anions selectivity. The monovalent anion selectivity stems from an increased electrostatic repulsion effect for divalent anions and hydrophilic property of the membrane surface. Remarkably, the separation efficiency of $\text{Cl}^-/\text{SO}_4^{2-}$ is increased from – 8.93% (unmodified AEM) to 94.43% (constructed 7.5 bilayers on the surface of AEM by electric-pulse deposition method) during 20 min and the permselectivity value is increased from 0.81 to 47.04. Compare to the traditional electrostatic deposition modification and the electro-deposition modification methods, the multilayer constructed by electric-pulse deposition technology with significantly homogeneous and stable monovalent selective separation multilayer. Besides, the modified AEM shows the higher selectivity than the commercial monovalent ion-selective AEMs.

1. Introduction

In natural systems, anions occur in hydrated condition; these hydrated anions play an important role in many chemical and biochemical processes [1–3]. Migration of mixed anions in a specific direction under an electric field is attracting attention as a separation technology, and many methods are explored to separate these mixed anions [4–7]. Materials with ion exchange capacity have been studied for removal or concentration of ions in water [8–10]. Anion exchange membranes (AEMs) offer a straightforward approach to separate anions from seawater, brackish water and industrial wastewater [11–15]. Besides, the AEMs also the key section in fuel cell [16–20].

However, the resulting solution is always a mixture of several types of anions, such as F^- , Br^- , Cl^- , NO_3^- , SO_4^{2-} . It is often necessary to remove the high concentration of anions such as F^- and NO_3^- , which may harmful for body [21]. On the other hand, nitrate can be a useful anion as well, which can be applied as a main source of nitrogen for plants. For Br^- , useful applications can be found in industrial production [22]. Thus, selective separation of anions is of high interest and the monovalent selective layers have potential for this purpose.

Ion channels and ion pumps have been designed to make a monovalent selective structure [23–26]. However, the preparation process is

complex and conditions are difficult to control in the separated solution. Recently, commercial membranes modified by cross-linking and deposition of polyanions were shown a selectivity for monovalent ions [27,28]. However, the high membrane area resistance of modification layers, poor stability of modified layers and the low efficiency of modification may limit the application of this kind of AEMs in the industry [29,30].

Alternating deposition of polycations and polyanions on ion exchange membranes is a method for synthesizing multilayer for anions separation [31]. For example, the electrostatic deposition layer-by-layer (LbL) assembly modification [32–34] and alternative electro-deposition LbL assembly modification [14] process to enhance the selectivity of ion transport has been reported in many studies. Although the electrostatic deposition LbL assembly modification method provides a convenient way to enhance the monovalent selectivity of a membrane, the low modification efficiency and instability of the assembled layers make such membranes unsuitable for application [35,36]. An alternative electro-deposition LbL assembly modification method can enhance the stability of the multilayer coated on the membrane, but it may lead to an inhomogeneous membrane surface [14]. The area resistance value of modified membrane is also the key property for ion exchange membrane, it depend on the modification materials or

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modification methods. Especially, the homogeneously modification methods, which can get rid of the redundant and accumulated modification materials further decreasing the resistance of modified membrane [14].

Here, a new approach was design for fabricating monovalent AEM, LbL assembly by electric-pulse deposition modification technique to construct multilayer on the membranes surface to solve the challenges of the above methods. The inspiration for this approach comes from the Chinese philosophy of Tai Chi, which considers two opposing principles in nature denoted as yin and yang, the former feminine and negative, the latter masculine and positive. The concept of Tai Chi elaborates the unity of opposites, being interdependent, well coordinated, transforming each other; it had been applied in many fields [37–39]. N-O-sulfonic acid benzyl chitosan (NSBC), a highly hydrophilic negatively charged chitosan suitable for selectively separating of hydrated anions or free anions [40]. Hydroxypropyltrimethyl ammonium chloride chitosan (HACC), a highly hydrophilic positively charged chitosan [41] was used for the LbL assembly of coating layers with NSBC by electric-pulse deposition technology.

In the current technology and materials, the highly hydrophilic polymers were chosen and 7.5 modification bilayers were homogeneously coated on a commercial AEM by electric-pulse technology to enhance the anion selectivity. The results show that the modified membrane with the separation efficiency as high as 94.43% and the permselectivity value is 47.04, which is higher than the commercial monovalent ion-selective AEMs. In addition, the monovalent selectivity and stability of the modified membrane by electric-pulse technology is higher than other modified membranes. This work illustrated the essential of the homogeneous modified technology and the results shows the modified membrane with the construction of monovalent selective separation multilayer by electric-pulse technology is attractive for monovalent anions selectivity in water separation.

2. Experimental section

2.1. Materials

The construction of a monovalent selective multilayer on the

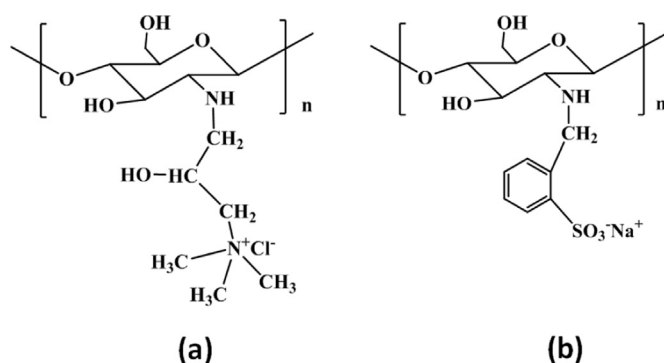


Fig. 1. The chemical structures of 2-hydroxypropyltrimethyl ammonium chloride chitosan (a) and N-O-sulfonic acid benzyl chitosan (b).

commercial AEM surface was based on the following polycations and polyanions: 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC), molecular weight (MW) = 20,000 g/mol obtained from Dongying Tianhua Co. (Shandong, China), and N-O-sulfonic acid benzyl chitosan (NSBC), synthesized in the laboratory (see below). The chemical structures of HACC and NSBC are shown in Fig. 1a and b, respectively. All chemicals were analytical reagents and have been used without pre-treatment. Chitosan (90%), 2-formylbenzenesulfonic acid sodium salt (95%), acetone (99.5%), sodium chloride (99.5%), sodium sulfate anhydrous (99%) and all other chemicals were obtained from Aladdin Industrial Co. Ltd. (Shanghai, China). The commercial homogeneous AEM-Type I and CEM-Type I were purchased from Fujifilm (Japan) and passed through an aqueous cleaning for the removal of surface preservatives before use. ACS monovalent ion-selective AEM (NEOSEPTA®, Japan), ASV monovalent ion-selective AEM (SELEMIION™, Japan) and AMX anion exchange membrane (NEOSEPTA®, Japan) are chose to compare with the modified AEM. Table 1 shows the properties of the different types of commercial AEM and CEM.

2.2. Synthesis of N-O-sulfonic acid benzyl chitosan

NSBC was synthesized according to the Schiff base formation reaction [42]. In a typical polymerization procedure, 2.50 g chitosan was dissolved in 100 mL 0.7 wt% aqueous acetic acid solution. After that, making the pH of mixed solution is 3.0 by 1 M HCl solution. Then 9.68 g 2-formylbenzenesulfonic acid sodium salt was dissolved in water (25 mL). Subsequently, the chitosan solution was drop-by-drop added into the above solution in about 20 min. Then the mixture solution was refluxed at 60 °C for 5 h. When the solution was cooled to room temperature, 1 M NaOH solution was added to adjust the pH to 5.0. Then 125 mL NaBH₄ solution (2.5% w/v) was added into the solution. Finally, 250 mL acetone was added to separate the white flocculent material. The obtained material was dried in a vacuum oven at 50 °C for 12 h. The reaction route for N-O-sulfonic acid benzyl chitosan is shown in Fig. 2.

2.3. Construction of monovalent selective separation layers

The commercial AEM was first rinsed with pure water to remove preservatives from the membrane surface. It was then stored in 0.50 M NaCl solution for 24 h. The commercial AEM (discs, 60 mm diameter) was placed into the experimental setup and the experimental electric-pulse deposition setup (as shown in Fig. S1 in Supporting information). Then, by electric-pulse deposition, NSBC and HACC layers are coated on the commercial AEM surface to construct separation layers with selectivity for monovalent anions. Due to the external electric-pulse force, NSBC and HACC are activated and show a powerful adsorption capacity. As a result, a homogeneous and stable multilayer is coated on one side of the AEM. The electric-pulse was provided by an electrochemical workstation (AUTOLAB AUT86804, the Netherlands). With the external electric-pulse force, negatively charged NSBC migrates intermittently to the unmodified AEM and combines with the quaternary ammonium cationic groups of the AEM. Scheme 1 shows the selected modification process with the electric-pulse technology. When

Table 1
Characteristics of the anion exchange membranes and cation exchange membrane^a.

Membranes type homogeneous	Thickness (μm)	Burst strength (kPa)	Area resistance (Ω cm ²)
AEM-Type I	125	2.4 (wet)	1.3
ACS monovalent ion-selective AEM	120–200	≥ 150 (dry)	3.0–6.0
ASV monovalent ion-selective AEM	120	200 (dry)	3.1
AMX anion exchange membrane	120–180	≥ 300 (dry)	2.0–3.5
CEM-Type I	135	2.7 (wet)	2.7

^a Commercial data.

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