



Rapid communication

Feasibility study on surface modification of cation exchange membranes by quaternized chitosan for improving its selectivity

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ABSTRACT

The feasibility that quaternized chitosan was used as cationic layer for surface modification of two kinds of commercial cation exchange membrane (CEM, one is heterogeneous and the other is homogeneous) to enhance their selectivity was reported in this paper. The membranes before and after modification were characterized by observation of surface morphology and determination of selective separation properties in detail, respectively. Scanning electron microscopy (SEM) displayed the difference of surface morphology induced by modification. The selectivity of membranes toward protons vs. metallic cations was investigated through electro dialysis experiments in binary systems (H^+/Zn^{2+} and H^+/Al^{3+}) and tertiary systems ($H^+/Zn^{2+}/Al^{3+}$). The results indicated that the transport of the metallic cations was decreased significantly after surface modification due to the electrostatic and steric barrier created by the thin cationic quaternized chitosan layer. In addition, the contrastive experiments such as the orientation of the modified layer (facing cathode or anode) were also carried out and analyzed tentatively.

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1. Introduction

Owing to the development for several decades, the electrochemical properties of ion exchange membrane have been vastly improved and some of them have attained almost limiting values [1]. However, there are still some requirements coming from some specific applications were expected to be met. For instance, in hydrometallurgy, separation of specific cations from the mixture together with acid recovery was often needed. Moreover, especially in some applications of water-splitting electro dialysis, it is important for keeping membrane performance to avoid the scale formation of bi-valent hydroxide and lessen membrane fouling. Obviously, one of the effective ways to implement the aforementioned expectations is endowing cation exchange membrane (CEM) the monovalent ion selectivity.

It has been confirmed for many times that a cation-exchange membrane modified by formation of a cationic layer on the membrane surface is preferentially permeable to cations of lower rather than higher valency and to smaller hydrated cations rather than larger ones due to the electrostatic repulsion and pore size sieving effect. According to literatures reported, the formation of

the cationic layer, apart from the chemical modification of base membrane material [2,3], mostly limited to several kinds of conducting polymers such as polypyrrole [1,4,5], polyaniline [6–11] and polyethyleneimine [12–14] though their modified methods were different from each other.

Recently, chitosan caught more and more attention from the technological and academic points of view because of its several outstanding characteristics such as low price, rich resources and environmental kindness. It, including its derivatives, has been used as separation membrane materials in microfiltration [15], ultrafiltration [16], nanofiltration [17,18], reverse osmosis [19,20], pervaporation [21–23], gas separation [24], etc. However, to the best of our knowledge, no one considers chitosan as a kind of surface modification material for ion exchange membranes.

In this work, a kind of strongly cationic quaternized chitosan layer was formed to endow commercial CEMs mono-valence ion selectivity by means of electrodeposition method. Besides the observation of surface morphology by SEM, the selective separating property of membranes with and without modification were determined through electro dialysis experiments in binary systems (H^+/Zn^{2+} and H^+/Al^{3+}) and tertiary system ($H^+/Zn^{2+}/Al^{3+}$). Moreover, the contrastive experiments such as the orientation of the modified layer (facing cathode or anode) were also performed and analyzed tentatively.

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2. Experimental

2.1. Materials and apparatus

2.1.1. Materials

Chitosan was supplied by Zhejiang Jinke Biochemistry Co. Ltd. 2,3-Epoxypropyltrimethyl ammonium chloride was purchased from Shandong Guofeng Fine Chemical Co. Ltd. The synthesizing method of quaternized chitosan was reported in our previous work [18]. NaCl, H₂SO₄, ZnSO₄, EDTA, K₂SO₄ and Al₂(SO₄)₃ were analytical grade chemicals and used directly without any purification. Indicators, EBT and XO, were newly prepared and stored under lower temperature. Heterogeneous and homogeneous CEMs were products of Qianqiu Environmental Protection Water Treatment Corporation (China) and Tianwei Membrane Technology Corporation (China), respectively.

2.1.2. Apparatus

Membrane surface morphology was observed by JSM-6700F scanning electron microscopy produced by electrical corporation of Japan. Electrodeposition modification and electro dialysis experiments were carried out using homemade facilities.

2.2. The modification of commercial CEMs

The sketch of electrodeposition apparatus, a three-compartment cell (effective membrane area: 5 cm × 5 cm; capacity: 200 ml) structure, was shown in Fig. 1. Among them, the middle compartment was filled with the mixture of 2 g/l quaternized chitosan solution and 0.1 M sodium chloride solution, and the other two compartments were all filled with 0.1 M sodium chloride solution as electrode solution. Two titanium electrodes coated by ruthenium were selected as cathode and anode. The electrodeposition time and current density were set as 2 h and 20 mA/cm², respectively. To avoid concentration polarization, constant stirring by peristaltic pump is necessary. All membranes prior to use were rinsed with distilled water to remove excess impurities. After finishing this experiment, modified membrane should be stored in 0.1 M sodium chloride solutions.

2.3. Scanning electron microscopy (SEM)

Membranes which were immersed in 0.1 M sodium chloride solutions were first dried under vacuum at room temperature in the presence of P₂O₅ for several days. Then, scanning electron microscopy could be taken after treated samples were sputtered with gold to ensure excellent conductivity.

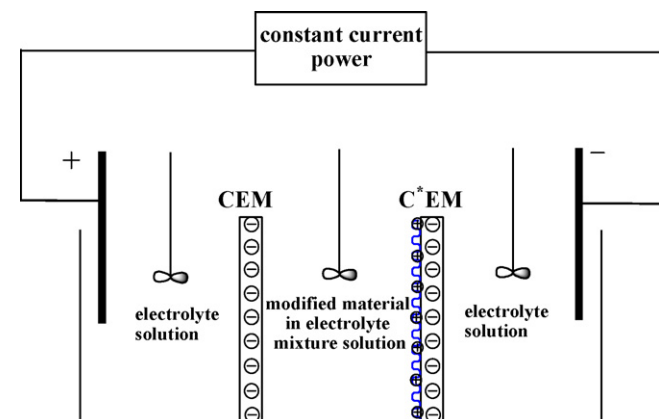


Fig. 1. Modification setup of CEMs using electrodeposition method.

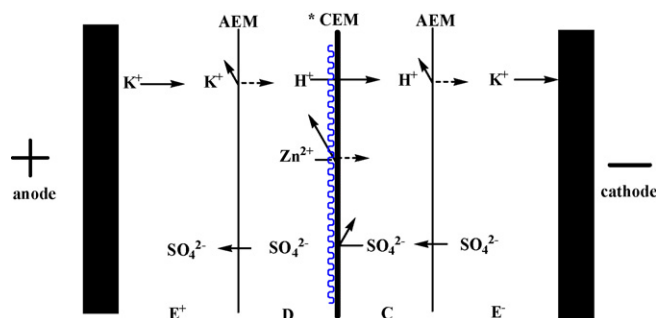


Fig. 2. Electro dialysis cell. D: dilute compartment; C: concentrated compartment; E⁺ and E⁻: electrode compartments.

2.4. Electro dialysis experiments

The experiments were performed in a four-compartment cell (effective membrane area: 5 cm × 5 cm; capacity: 200 ml) electro dialysis setup displayed in Fig. 2. The dilute compartment and concentrated compartment were fed with the mixture of 0.5 M H₂SO₄ solution and salt solution with specified concentration such as 15 g/l ZnSO₄, 16 g/l Al₂(SO₄)₃ or their mixture, respectively. Stainless steel electrode and titanium electrode coated by ruthenium were chosen as anode and cathode, respectively, in order to avoid the falling of ruthenium thin layer because of oxygen-releasing reaction taking place near the anode. And, 0.5 M K₂SO₄ solution instead of H₂SO₄ was chose as electrode solution to avoid dissolution of stainless steel. Electro dialysis time and current density were set as 100 min and 20 mA/cm², respectively. Metal ion concentration was determined by EDTA complexometry titration. The value of %Mⁿ⁺ leakage was calculated according to the following equation:

$$\%M^{n+} \text{ leakage} = \frac{\text{mass of } M^{n+} \text{ in concentrated cell}}{\text{mass of } M^{n+} \text{ in concentrated and dilute cells}} \times 100 \quad (1)$$

3. Results and discussions

3.1. The modification of commercial CEMs

In this research, the cationic quaternized chitosan layer was formed on surface of CEMs by means of electrodeposition method. This is based on the fact that quaternized chitosan molecules with positive charges will migrate directly toward cathode when a direct current field was exerted. Due to their high molecular weights and small pore size of membrane, these macro-ions could not cross the membrane and finally deposit on surface of the membrane facing anode. Obviously, the formation of modified layer was controllable to some extent through adjusting the relevant parameters such as concentration of modified materials, electrodeposition time, current density, and so on.

Membrane surface morphology was observed by SEM and displayed in Fig. 3. From these pictures, it can be seen clearly that the membrane surface after modification becomes rougher compared with that of unmodified membrane. Additionally, a fact was also found that small pores previously appearing in unmodified membrane almost diminished on surface of modified membrane, which means that these pores might be covered with the modified layer. These experimental results similar to the ones observed by Sophie et al. [8] confirmed the existence of quaternized chitosan layer. Similarly, the relevant outcome of homogeneous membrane was also achieved and not provided here.

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