



Composite anion exchange membrane made by layer-by-layer method for selective ion separation and water migration control



Yufei Zhang^{a,b,d}, Ru Liu^{a,b,d}, Qiaolin Lang^{a,c}, Ming Tan^{a,c,*}, Yang Zhang^{a,c,*}

^a Waste Valorization and Water Reuse Group (WVWR), Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Laoshan District, Qingdao 266101, China

^b State Key Laboratory of Petroleum Pollution Control, Beijing 102206, China

^c Qingdao Key Laboratory of Functional Membrane Material and Membrane Technology, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

^d University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China

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ABSTRACT

In ion exchange membrane processes (e.g. electrodialysis), improving ion selectivity and reducing water permeance are two key concerns, which drive new membrane fabrication methods. Preparation of composite ion exchange membrane with functional layers may be a solution to elevate its performance. In this study, composite anion exchange membranes (C-AEM) were prepared by using layer-by-layer (LbL) method, and were characterized with regard to membrane surface properties, selectivity, as well as water permeance. Results indicate that monovalent ion selectivity increased with the number of assembled layers. More specifically, when the membrane was modified with 10.5 layers, $P_{SO_4^{2-}}^{Cl^-}$ reached over 10, which was much higher than the commercially available monovalent selective membrane (ACS, $P_{SO_4^{2-}}^{Cl^-}$ around 5). Besides, the C-AEMs also showed a good performance on organic ion selectivity and water migration control. This work proves that LbL method is an effective way to prepare functionalized ion exchange membrane by controlling membrane surface properties (surface potential and pore size). Furthermore, this work provides an investigation of transport mechanisms of ions with different charge, different size and different hydration number by penetrating functional membranes with layered top structure. The prepared C-AEMs showed a good separation efficiency of monovalent ions and organic acids with controlled water migration, this may be potentially used in desalination, wastewater treatment, chemical separation, or other related fields.

1. Introduction

As the improvement of membrane material and fabrication techniques, a series of membrane processes driven by pressure difference, concentration difference and potential difference, play a vital role in the separation, enrichment, purification and other applications [1]. As an electro-driven membrane process, electrodialysis (ED) employs ion exchange membranes for ion separation, which has been proven as an emerging technology to separate salt and charged molecules from water [2–4]. The related electrodialysis applications can be found in various fields such as waste acid recovery [5], brine reclamation [6], and fermentation engineering [7].

However, functional ion exchange membranes are required in some specific applications, e.g. membranes with monovalent selective properties used for production of table salts from seawater [8,9], or membranes with different cavity sizes applied to purify organic acids with

various molecular weight [10,11]. The general principle of mono/divalent ions separation attributes to two mechanisms, i.e., steric-hindrance and electrostatics repulsion [12]. More specifically, the separation factor depends on the hydrated size of the ions, the hydrophilicity of the membrane and the charge on the membrane surface [2].

To date, different approaches to fabricate monovalent selective anion exchange membrane (AEM) have been reported. For example, formation of a highly cross-linked layer on the membrane surface has been reported to be an effective method [13]. However, the rigid structure would inevitably increase the electrical resistance. The formation of condensation-type polyelectrolyte [14] and weakly basic anion exchange group layer [15], as well as the hydrophilicity according to the anionic species [2,16,17], all hinder the improvement of ion selectivity. Commercially available monovalent anion selective membranes such as ACS (Astom, Japan) have been widely used in

* Corresponding authors.

E-mail addresses: tanning@qibebt.ac.cn (M. Tan), zhangyang@qibebt.ac.cn (Y. Zhang).

practical applications [18]. However, the separation factor $P_{Cl^-}^{SO_4^{2-}}$ is about 0.4, which still needs further development to fractionate salts with higher purity [19].

A promising approach has been proposed in which the membrane surface is modified with a thin and charged layer. It is reported that monovalent anion selective membranes with anionic polyelectrolytes, such as poly (sodium 4-styrene sulfonate) [19], polydopamine [20] and poly-vinyl-sulfate [21] have been fabricated, but the permselectivity of these membranes ($P_{Cl^-}^{SO_4^{2-}}$) were ranging from 0.4 to 0.22, which was still not enough to achieve an efficient separation of sulfate from chloride. A method with layer-by-layer (LbL) assembly of polyelectrolyte multilayers was found to be a good alternative [21]. In this method, alternating adsorption of polycations and polyanions on AMX (Astom, Japan) membrane leads to a high monovalent/divalent anions permselectivity with an odd number of LbL layers (poly sodium-p-styrenesulfonate top layer) above 15 [19]. It was reported that the amount of negative charge increases with increasing numbers of layers [22,23].

On the other hand, separation of organic ions is highly needed in fermentation and chemical synthesis industries [24]. The mechanisms of organic acids separation by functional membrane are mainly explained size exclusion, electrostatic repulsion and hydrophobic/hydrophilic adsorption.

Molecular size and charge number effects were mostly investigated in organic ion transport through ion exchange membranes in electro-dialysis [24]. Moon and the co-workers [24] reported separation of mixed organic ions by electro-dialysis with standard and monovalent selective membranes. Results showed that binary organic ion (succinate) can be separated from formate or acetate through monovalent selective anion exchange membrane due to size exclusion and electrostatic repulsion. However, it is difficult to separate organic ions with the same charge number [24].

Zhang et al. [25] reported that aspartate was removed faster than butyrate, which attributed to the hydrophobic/hydrophilic adsorption. Takahashi et al. [26] also explained the transport mechanisms of single, binary, and ternary acids in view of the hydrophobic/hydrophilic interaction between organic ions and the membrane surface. Huang et al. reviewed various electrically driven membrane processes in production of organic acids by electro-dialysis, and pointed out that although ED has shown competence in this field, development of specific selective ion exchange membranes for separating organic ions is an important goal [25].

Water co-transport with salts in electro-dialysis is another important issue need to be solved. As the ions exist as hydrated forms in aqueous solution, ion migration in electro-dialysis always result in water volume increase in the concentrate, this hinders further concentration of salt. Han et al. [27] calculated hydration number of four ions (Na^+ , Mg^{2+} , Cl^- , SO_4^{2-}) by using volume difference in the concentrate after electro-dialysis process. Results showed that the hydration number of sodium, magnesium, chloride and sulfate ions was 6, 15–16, 8, 13–14, respectively. A similar work had been done by Jiang et al. [28], they investigated water electro-transport with hydrated cations in ED. The work indicated that water electro-transport is significant and cannot be ignored. The authors also suggested that ion exchange membrane should be designed to mitigate water electro-transport by reducing hydrophilicity or increasing membrane cross-linkage (i.e., to make a “more dense” membrane).

As discussed above, ion hydration numbers not only influence ED

performance, but also significantly affect ion selectivity, since a higher hydration number result in a larger hydrated ionic size. As addressed, the hydration number of bivalent ions is much higher than that of monovalent ions, this induces a selectivity between monovalent and bivalent ions by ion exchange membranes in view of steric hindrance effect [27]. With regard to the commercially available ion exchange membranes, development of membranes with effectively retain water co-transport function is still in a gap for research and development.

Although LbL deposition method has been extensively used for NF and RO membrane modification to increase their performance [28–30], it has not yet well established for functionalization of ion exchange membranes. Furthermore, since LbL method controls membrane surface charge and top-layer “tightness”, it gives a possibility to separate ions and reduce water migration by adjusting layers and cross-linkage.

Therefore, composite anion exchange membranes (C-AEM) prepared by LbL method are investigated in this work. Monovalent anion selectivity, organic ion separation efficiency and control of water co-transport are further investigated with regard to the coated layers, and compared with the base membrane and the commercial monovalent anion selective membrane. Functionalization of ion exchange membrane by layer-by-layer method is further discussed to explore a capable way to improve electro-driven membrane separation and purification efficiency.

2. Experimental

2.1. Materials and chemicals

A homogeneous TWEDA1 standard anion exchange membrane was used as the base membrane (Tianwei Membrane Technology Co., Ltd., Weifang, China). Membrane properties of TWEDA1 membrane and PC-SK membrane (PCA GmbH, Heusweiler, Germany) were shown in Table 1 (data were provided by the manufacturer). In the electro-dialysis experiments, PC-SK membrane was used as a cation exchange membrane (CEM). The polyelectrolytes coating solution, poly (sodium-p-styrenesulfonate) (PSS, $M_w = 80,000$, 20 wt% aqueous solution) and poly (diallyldimethylammonium chloride) solution (PDDA, $M_w < 1,00,000$, 35 wt% aqueous solution), were provide by Shanghai Macklin Biochemical Co., Ltd. Industrial grade graphene aqueous slurry (TNIGNP content 5.0 wt%; dispersant 1.5 wt%; H_2O content 93.5 wt%; layers < 30) was bought from Chengdu Organic Chemicals Co., Ltd.

To investigate monovalent anion selectivity of the membranes, sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were used as the monovalent and divalent salts. In organic separation experiments, formic acid (AR, 88%) and hexanoic acid (> 99.5%, Aladdin biological technology Co. Ltd., Shanghai, China) were used. Besides, the sodium sulfate, sodium chloride, sodium hydroxide (NaOH) and hydrochloric acid (HCl) (purity $\geq 98\%$) were all analytical grade reagents (purchased from the Sinopharm Chemical Reagent Co., Ltd., China) without purification.

2.2. Membrane preparation

The PSS and PDDA solutions used for surface modification were prepared by dissolving 1 g/L of PSS or PDDA with 1 M NaCl (as a supporting electrolyte) in deionized water. To reduce the electrical resistance caused by the coated layers, graphene was dissolved in PDDA solution with different proportion from 0 to 10 wt%. Before the AEM

Table 1
The properties of ion exchange membrane used in the experiments.

Membrane	Thickness (μm)	Ion exchange capacity (mequiv./g)	Chemical stability (pH)	Water content (wt%)	Functional groups	Area resistance ($\Omega \cdot cm^2$)
TWEDA1	10–50	0.9–1.1	1–12	15–20	-NR ₄ Cl	≤ 2.50
PC-SK	160–200	c.a. 1	0–11	~9	-SO ₃ Na	2.50

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