

Preparation and Monovalent Selective Properties of Multilayer Polyelectrolyte Modified Cation-Exchange Membranes

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ABSTRACT: This study reports the modification of commercial cation-exchange membrane by layer-by-layer adsorption of polyethyleneimine and poly(acrylic acid) (PAA) to endow them with monovalent ion selectivity. The chemical and morphological changes of the modified membrane surface were examined by ATR-FTIR and SEM, respectively. The permselectivity for monovalent cations of the membranes was investigated by electrodialysis experiments. The effects of deposited bilayer number, the salt concentration, and pH of the dipping polyelectrolyte solutions on selectivity were investigated. Meanwhile, the resistance of membranes was measured taking energy consumption into consideration. The polyelectrolyte multilayer was crosslinked using epichlorohydrin to improve stability, and the durability of the composite membrane was studied. Separation mechanism of the composite membrane was also investigated. It is demonstrated that the bivalent cations are mainly rejected by electrostatic repulsion from the positive charge on the surface of the composite membranes. The sieving effect of the dense structure of skin layer becomes more pronounced with the number of deposited layers increased. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41488.

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INTRODUCTION

Electrodialysis (ED) with ion-exchange membranes (IEM) is widely used in desalination and concentration of salt solution because IEM can separate cations from anions.^{1,2} If IEM with monovalent ion permselectivity are developed, the utilization of ED can be further expanded to areas of integrated utilization of seawater,^{3–5} nitrate or hardness removal from drinking water,^{6,7} and waste acid recovery,⁸ etc.

Surface modification of IEM is an effective way to prepare monovalent ion selectivity membranes.^{9,10} Forming a layer with dense structure or proper charge on the surface of IEM both can improve the monovalent selectivity. A dense structure on the surface of membranes would retard the transport of larger multivalent ions. Conducting polymers such as polypyrrole and polyaniline were used to prepare monovalent selective cation-exchange membrane (CEM) because they formed compact structure on CEM.^{11,12} Alternatively, when a charged skin layer is deposited on IEM, it would be difficult for multivalent counterions to permeate into the support membrane, thus the monovalent selectivity is improved. For example, positively charged polymers such as polyethyleneimine (PEI)^{13–15} and quaternized chitosan^{16,17} were attached to the surface of CEM to prepare composite membranes with monovalent selectivity. The prepared membrane exhibit favorable monovalent ion selectiv-

ity, but the deterioration of the adsorbed film makes the membrane unstable in ED process.¹⁸

Alternating deposition of polycations and polyanions on substrate has been proven to be a low-cost and versatile technology to fabricate composite membranes with ultrathin skin.^{19,20} This method provides a convenient way to control over both compactness and surface charge density of membranes. It was reported that nanofiltration membranes with polyelectrolyte multilayer exhibits good selectivity toward monovalent ions against bivalent ions.^{21–23} Although several research groups modified IEM using this method recently, they mainly focused on the antifouling abilities of the prepared membrane.^{24,25}

In the present paper, we deposited PEI and poly(acrylic acid) (PAA) alternatively on a commercial CEM and the selectivity of the composite membranes was investigated by ED with solution containing sodium, calcium and magnesium ions as feed. The relationship between the monovalent selectivity and deposition conditions such as pH, NaCl concentration, and the number of adsorbed layers was discussed. The effect of layer number on the resistance of the prepared membrane was studied, since energy consumption must be considered in ED. The polyelectrolyte multilayer was crosslinked using epichlorohydrin (ECH) to improve stability, and the durability of the multilayer membrane was studied.

Table I. Some Characteristics of the CEM Used in This Work^a

Exchanger groups	Sulfoacid
Thickness (wet; mm)	0.3 ± 0.02
Water content (%)	33
Exchange capacity (dry; meq/g)	2
Electric resistance (Ω cm ²)	3.8
Current density (mA cm ⁻²)	<100

^a The parameters were provided by the manufacturer.

EXPERIMENTAL

Materials and Methods

The CEM with characteristics listed in Table I was supplied by Zhejiang Qianqiu Environmental Water Treatment (LE-HoCM-I-ZZ-SH). PEI solution (50 wt %, $M_w = 70,000$) was purchased from Aladdin Industrial Corporation. PAA (25 wt %, $M_w = 240,000$) was purchased from ACROS. Sodium chloride (NaCl), magnesium chloride, calcium chloride, and sodium sulfate (Na₂SO₄) were obtained from Tianjin DaMao Chemical Reagent Factory. The chromogenic reagent such as Cal-Red, eriochrome black T were provided by Tianjin Guangfu Fine Chemical Research Institute. These chemicals were all used as received without further purification.

SEM (Model S-4800, Hitachi, Japan) was used to characterize the surface topography of the composite membrane. The information of the chemical bonds and functional groups on the surface of the membrane was obtained by FTIR (Hss-tensor27, Bruker, Germany). Hydrophilicity/hydrophobicity of the membrane surface was analyzed by measuring the water contact angle using SL200B contact angle meter (ShangHai Solon).

Membrane Modification

The CEM was immersed in 0.1M hydrochloric acid for 24 h and rinsed with water before layer-by-layer deposition. PEI was deposited to the CEM by immersing the membrane in an aqueous solution containing 3 g/L PEI and NaCl for 15 min. Then PAA was deposited by exposed membrane to aqueous solution containing 3 g/L PAA and NaCl for 15 min. After every deposition process, the membrane was rinsed using distilled water. The alternative deposition of PEI and PAA was repeated until required number of bilayers was achieved. To improve the stability of the multilayer membrane, chemical crosslinking was conducted by immersing the membranes in ethanol solution of 2.5 g/L ECH at pH 9 for 60 min after polyelectrolyte deposition.

For multilayer membrane, “layer” usually refers to the polymer deposited after exposure to one of the polyelectrolyte solutions and “bilayer” is used to describe a pair of negative/positive polymer layers.^{26,27} Therefore, half bilayer as “2.5 bilayer” in this article refers to the membrane had two PEI/PAA bilayer and terminated with another PEI layer. The PAA terminated membrane had integer bilayers.

Permselectivity Measurement

The permselectivity measurement of the fabricated membrane was conducted on a home-made ED apparatus as shown in Fig-

ure 1. The membrane sample was fixed in the middle of the four chambers and the other two auxiliary membranes were both anion-exchange membranes to prevent leakage of cations. Solution with sodium ion, calcium ion and magnesium ion at a concentration of twice of seawater was selected as feed solution. All the anions were chloride ions to avoid the influence of anions on the selectivity. One hundred and seventy milliliters of feed solution and 0.2M NaCl were injected into the dilute chamber and the concentrating chamber, respectively. In addition, 0.2M Na₂SO₄ solutions were used as electrode solution for both cathode and anode. After a 60-min ED experiment at current density of 16 mA/cm², the concentration of divalent cations and chloride ion in concentrating chamber was measured by titrating. The concentration of sodium ion was calculated by charge balance.

The monovalence selectivity of the membrane was characterized by calculating the separation efficiency (*S*) according to the equation^{7,28}

$$S(\%) = \frac{C_{II}/C_{II0} - C_I/C_{I0}}{(1 - C_{II}/C_{II0}) + (1 - C_I/C_{I0})}$$

where C_I and C_{II} are the concentrations of bivalent and monovalent cations in the dilute phase, and C_{I0} and C_{II0} are the initial concentrations of monovalent and bivalent cations in the feed solution, respectively. In this article, the monovalent ion refers to sodium ion, and the concentration of bivalent cation is a sum of calcium ion and magnesium ion. The separation efficiency is independent of the experimental conditions and ranges from 0 (no separation) to 1 (complete separation).⁷

Membrane Resistance Measurement

The resistance for ion transport of these composite membranes in traverse direction was measured using AC impedance technique. The measurement cell consists of two stainless steel electrodes with a contacting area of 32.2 mm² and a sealed container made of insulated material to maintain humidity of the membrane. The membrane to be tested was fixed between the two electrodes, which were connected to an Advanced Electrochemical System (AES, PARSTAT 2273) through copper wires. The resistance was derived from the low intersection of the high frequency semi-circle with the Re(*z*) axis on a electrochemical impedance spectroscopy.

RESULTS AND DISCUSSION

Characterization of the Modified Membrane

ATR-FTIR Spectra. Figure 2 shows the ATR-FTIR spectra of the cation-exchange support membrane and the modified membrane with four bilayers. Compared with the spectrum of pristine CEM, the spectrum of 4-bilayer polyelectrolyte modified membranes has the peaks associated to the carboxylic acid groups (1550 cm⁻¹), indicating successful deposition of PAA. The peak at 1080 cm⁻¹ in the spectra of modified membranes was assigned to the bend vibration of C—N, indicating the existence of PEI. Moreover, the characteristic bands for sulfonic acid groups at 1008, 1038, and 1175 cm⁻¹ did not shift or decrease significantly after the polyelectrolyte deposited, demonstrating that the modification process had little influence on the ion conductivity of the support membrane.

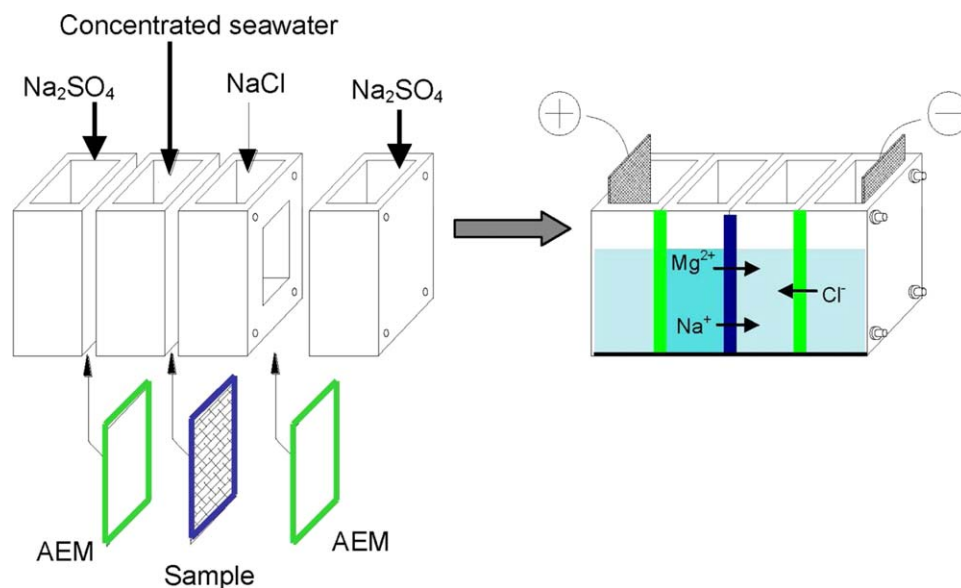


Figure 1. Diagram of ED experiment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEM Images. To further verify the deposition of PEI and PAA, membrane surface morphology was observed by SEM and displayed in Figure 3. Obvious difference was detected from the two pictures with same magnification. The support membrane showed a uniform surface with some tiny flake shaped bulge. After deposition, most part of the surface became smoother and some grains of polyelectrolyte were observed.

Surface Hydrophilicity. Water contact angles were measured with PEI and PAA as the terminating layer and the results are displayed in Figure 4. The contact angles of the modified membrane vary with the type of polymer on the surface of the membrane. The unmodified CEM exhibited an average contact angle of 85.1° , and this value sharply decreased to 48.3° when the

membrane was deposited with a layer of PEI. Moreover, the contact angle was further decreased to 34.3° after deposition of the first layer of PAA. In the later deposition, the contact angle changed alternately with the alternate deposition of cationic and anionic polyelectrolyte. With the increment of bilayer number, the PAA terminated membrane surface was more hydrophilic, whereas the PEI terminated membranes was more hydrophobic. All the tested membranes showed smaller contact angle compared with the unmodified CEM, suggesting that the multilayer membranes become more hydrophilic.

Effect of the Bilayer Number on Separation Performance and Resistance

In general, the sieving effect from the skin layer can be regulated by the number of deposited layers. Selective coefficient of the membranes with different layer is depicted in Figure 5. The pristine CEM showed a selective coefficient of 0.001 indicating it had no permselectivity for cations with different valent. The structures formed by layer-by-layer assembly are dense, as a result of the strong electrostatic bonding within the multilayers. Assuming that the rejection of multivalent ions is due to sieving effect, the separation efficiency should increase with the number of polyelectrolyte layers. As shown in Figure 5, there was an obvious increase in selectivity with the deposition of initial three layers as expected. However, further deposition of PAA reduced the selectivity of the composite membrane. With more bilayers deposited, the PEI terminated membranes showed higher separation efficiency value compared to membranes with one more layer of PAA deposited on. This clearly indicated that in addition to thickness, electrostatic repulsion afforded by the positively charged PEI played a more important role in selectivity of multilayer polyelectrolyte composite membranes.

Figure 6 displays the resistance and selectivity for ion migration of PEI terminated membranes with different bilayers. The selective coefficient of membranes increased dramatically with the

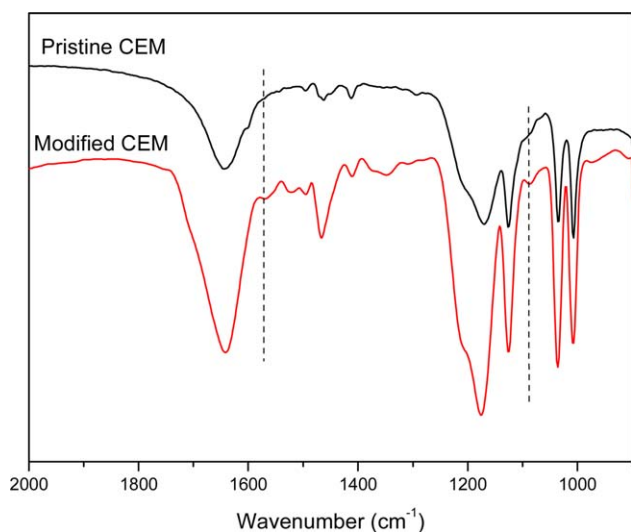


Figure 2. ATR-FTIR spectra of pristine CEM and multilayer polyelectrolyte modified CEM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

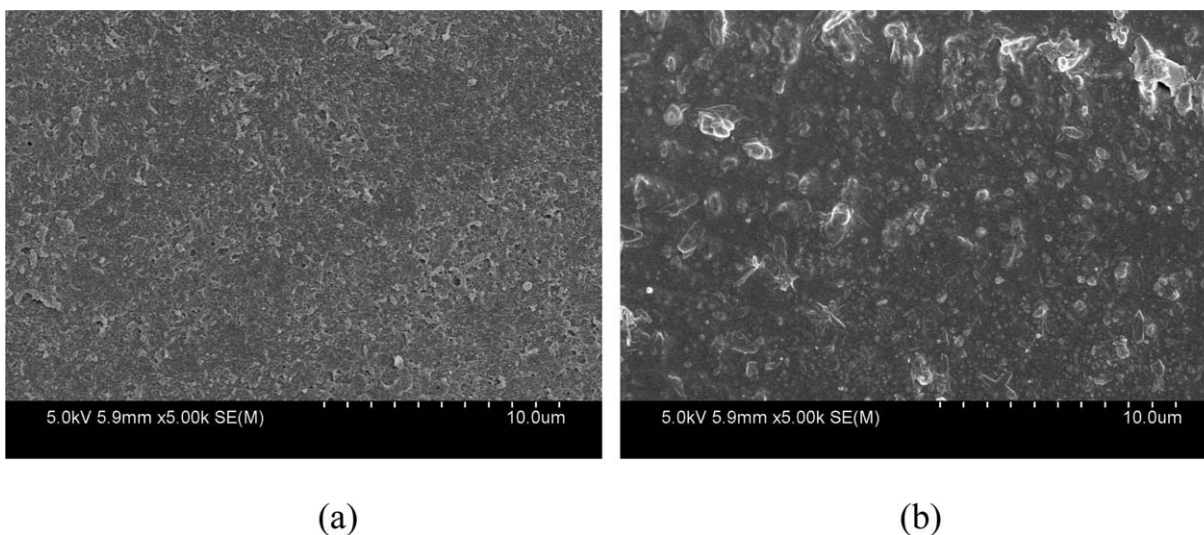


Figure 3. SEM images of (a) pristine CEM and (b) multilayer polyelectrolyte modified CEM.

deposition of the first 1.5 bilayers, but showed a slight increase with further deposition. It seems that the initial three polyelectrolyte layers on the CEM were thicker than the subsequent layers. This is not in accordance with early studies^{29,30} that the PEI/PAA multilayer films grow exponentially in the first several bilayers. We believe it was mainly due to the different substrates for polyelectrolyte adsorption. The silicon or quartz substrate offered a low charge density surface and resulted in thin initial layers. The exponential growth of the later layers was due to the interdiffusion and interaction of PEI and PAA.³¹ Compared with the inorganic substrates, CEM provided significantly high charge density from sulfonic acid groups, which was considerably effective for polyelectrolyte adsorption and caused a thicker layer just on the surface of the CEM.

CEMs show good ion transportation property for their high density of ion-exchange groups. It was reported that ions transport through multilayer polyelectrolyte films by hopping between ion-exchange sites,^{32,33} which is similar with that in a

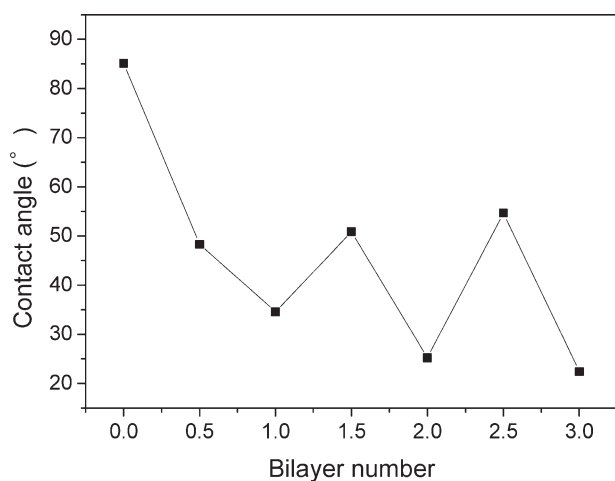


Figure 4. Change of contact angle of multilayer membrane with bilayer number. (Membranes with half bilayer number were terminated with PEI and the integer bilayer number membranes are terminated with PAA.)

ion-exchange membrane. After deposition and crosslinking, a high network density was achieved on the surface of the CEM and made the ion channel more narrow, which induce good selectivity for cations of different size. However, this compact layer hindered the transport of all the ions. Therefore, the resistance of the modified membrane was heightened significantly with the first layer of PEI adsorbed and then showed a modest increase with the polyelectrolyte bilayer number (Figure 6). It was also noted from Figure 6 that after 2.5 bilayers of deposition, further deposition resulted in near linear increase in resistance while slight improvement of selectivity. Meanwhile, the value of selective coefficient reached to 0.73 at this bilayer number. Therefore, 2.5 bilayers of deposition were selected for all the monovalent selective membrane fabrication in this study.

Effect of NaCl Concentration of the Dipping Solution on Selectivity

Multilayer membranes were prepared with NaCl concentrations in the dipping solution varied from 0.1 to 1.0M and the

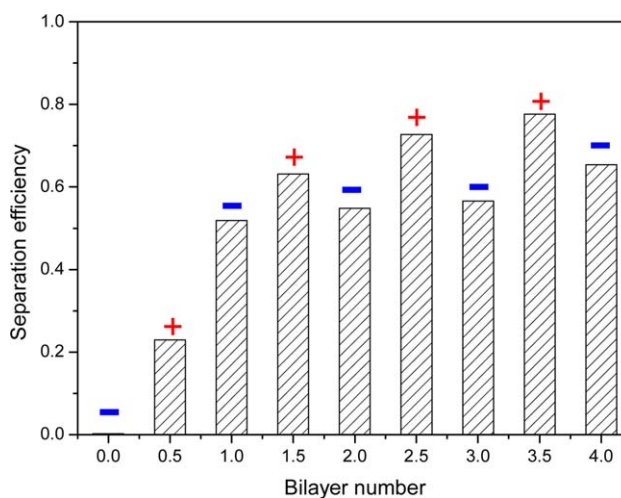


Figure 5. Effect of bilayer number on separation efficiency of membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

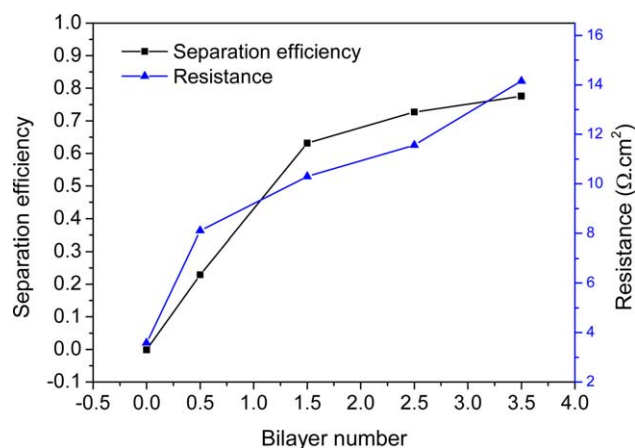


Figure 6. Effect of bilayer numbers on separation efficiency and resistance of membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

separation efficiency of the membranes is displayed in Figure 7. In solution without NaCl, both PEI and PAA chains are unfolded at the mutual electrostatic repulsion of the polymer chains. The addition of salt strongly reduced this repulsion and the polymer chains gradually become coils so that they are rather easy to be adsorbed. Consequently, the density of the deposited monolayer increases. As expected, the monovalent selectivity and resistance for ion migration of the membranes were both increased with the salt concentration. Considering better selectivity and energy saving during ED together, 0.5M NaCl in the PEI or PAA solution was performed in following experiments.

Effect of pH of the Dipping Solution on Selectivity

For weak polyelectrolyte as PEI and PAA, pH value of the solutions dramatically affects the assembly behavior and finally influences the selectivity of the multilayer membrane. The PEI and PAA solutions of 3 g/L were at pH 10.8 and pH 2.9, respectively. With acid added, amine groups of PEI and carboxyl groups of PAA both tended to be protonated.^{29,34} This made more PEI molecules present as positively charged state while

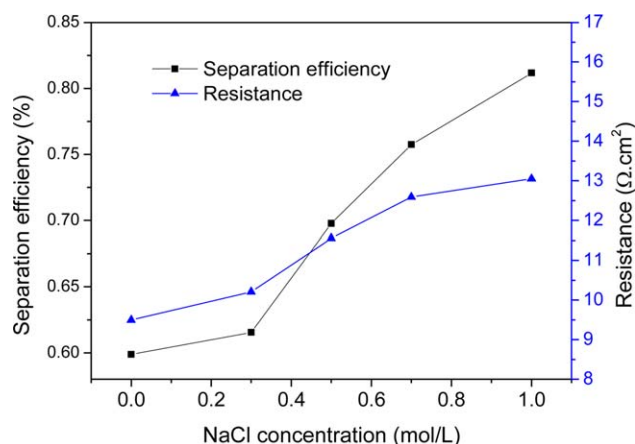


Figure 7. Effect of NaCl concentration on separation efficiency and resistance of membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

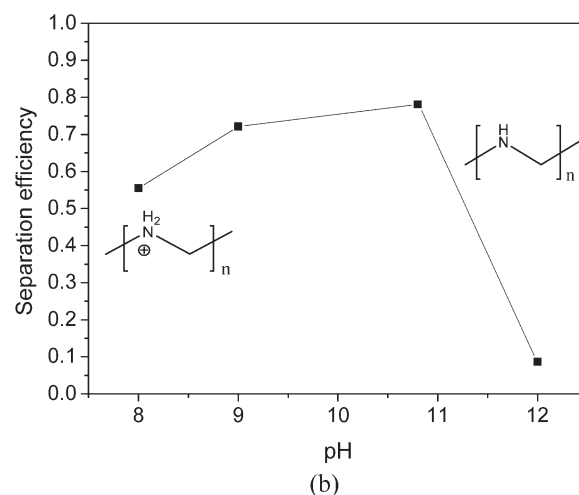
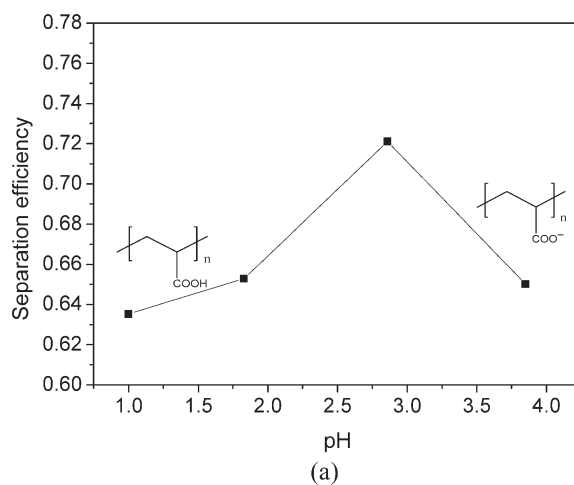


Figure 8. Effect of pH of (a) PAA solution (b) PEI solution on separation efficiency of membranes.

PAA tended to be present in non-ionized state. Addition of alkaline resulted in opposite effect. Since the interaction between PEI and PAA was induced by electrostatic attraction, a lower ionized degree led more polyelectrolyte be adsorbed to neutralize the opposite charge on the surface of the membrane. However, it has been reported that the deposited polyelectrolyte with too much nonionized segments would induce loose structure and larger mesh size in the skin layer.³⁵ As a result, ion selectivity caused by size difference was reduced. As a consequence of the two opposite effects, the separation efficiency of the prepared membrane presented a peak as displayed in Figure 8. At pH of 2.9 for PAA and 10.8 for PEI, the prepared membrane showed best selectivity.

Separation Mechanism Analysis

To investigate the separation mechanism of the multilayer polyelectrolyte modified CEM, the PEI terminated multilayer membranes were immersed in 0.1M hydrochloric acid or 0.1M ammonia solution before ED and the separation efficiency is shown in Figure 9. With the increase of bilayer number, the separation efficiency increased from 0.23 to 0.71 for membranes equilibrated with hydrochloric acid, while this value ranges

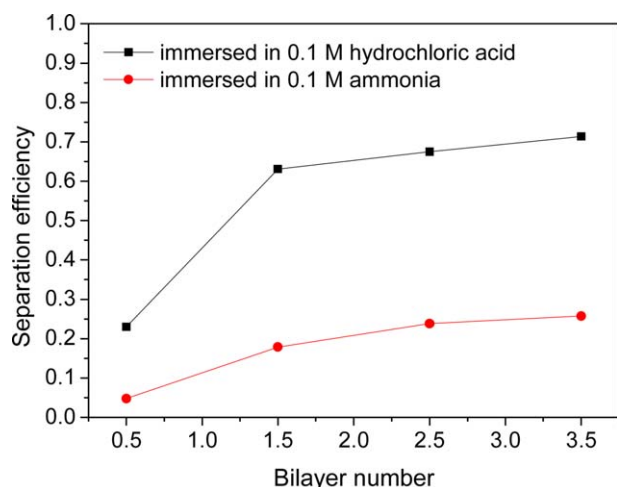


Figure 9. Effect of equilibrium solution on separation efficiency of membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from 0.048 to 0.26 for that equilibrated with ammonia. Specifically, at similar sodium ion fluxes, the permeated bivalent cations through membranes equilibrated with hydrochloric acid are about one-third of that equilibrated with ammonia solution. The difference is only caused by the change of charge density on the skin layer, which is affected by pH. It confirmed that the increase in separation efficiency is mainly due to the difference of electrostatic force to cations with different valence.

If the electrostatic repulsion from every layer of PEI in the multilayer is effective for ions separation, the membrane equilibrated with acid would provide a more pronounced repulsion than that equilibrated with ammonia with the bilayer number. However, as seen in Figure 9, the trends of the two lines are very similar suggesting the increase of separation efficiency with bilayer number is mainly caused by the increased structural density. Only the PEI molecular on the surface of the membrane provided positive charge and favored the selective separation of monovalent and divalent cations. Most of the PEI in the multilayer interacted with PAA and could not provide electrostatic repulsion to the cations even treated with acid.

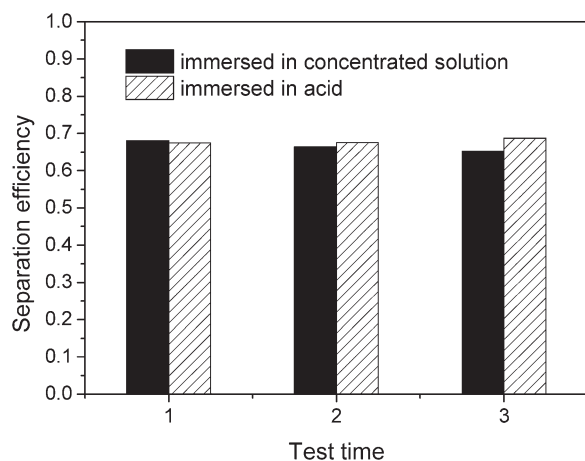


Figure 10. Durability of composite membranes in concentrated solution and acid.

Therefore, the enhanced selectivity of the multilayer polyelectrolyte modified CEM is the result of two effects: an electrostatic repulsion from PEI on the surface of the composite membrane as well as increased structure density from the polyelectrolyte multilayer. Monovalent selectivity is mainly caused by electrostatic repulsion from the membrane surface and the sieving effect of from dense structure of skin layer becomes more pronounced with the number of deposited layers increased.

Durability of Multilayer Polyelectrolyte Composite Membrane

After layer-by-layer deposition and crosslinked with ECH, the multilayer polyelectrolyte composite membranes were expected to show good stability. The durability of the membranes was examined by measuring the separation efficiency after the membrane was immersed in concentrated salt solution and 0.1M hydrochloric acid for every 24 h. Figure 10 displays the results. The separation efficiency of composite membrane with 2.5 bilayers did not decline markedly after every 24 h immersing in concentrated solution and hydrochloric acid. These results suggested that monovalent ion permselectivity was maintained for long-term ED process. After 3-day immersion, both membranes exhibit separation efficiency >0.65 , which indicate good stability of the multilayer polyelectrolyte composite membranes.

CONCLUSION

Monovalent selective multilayer membranes were fabricated by alternating deposition of PEI and PAA on CEM followed by crosslinking with ECH. The mono-bivalent selectivity was improved with the deposited bilayer number, while the resistance for ion permeation was increased simultaneously. Increasing the salt concentration of the dipping solution favored the selectivity of modified membranes. Therefore, 2.5-bilayers composite membranes prepared in 0.5M NaCl solution were selected for monovalent ion separation in this article. The optimal pH of the deposition solutions was 10.8 and 2.9 for PEI and PAA, respectively. Monovalent selectivity is mainly caused by electrostatic repulsion from the membrane surface and the sieving effect of from dense structure of skin layer becomes more pronounced with the number of deposited layers increased. After crosslinking, the multilayer polyelectrolyte modified membranes showed long-term stable separation efficiency >0.65 , which indicate good durability for monovalent ion selectively separation. It was demonstrated that modifying the cation-change membrane by multilayer polyelectrolyte is a suitable method to prepare monovalent/bivalent cation selective membranes.

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