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A modified coating method for preparing a mono-valent perm-selective cation exchange membrane: I. The evolution of membrane property corresponding to different preparing stages

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ABSTRACT

In this work, enlightened by the preparation of the Tokuyama BP-1 bipolar membrane, a modified coating method is attempted to prepare the mono-valent perm-selective cation exchange membrane (CEM). That is, a surface-roughening step is introduced into conventional coating technology to increase the contacting area and strengthen the interaction between modification layer and base membrane. Furthermore, a post-quaternization is carried out after the formation of the cross-linked chitosan layer to weaken the effect of the electrostatic repulsion among the cationic charged macromolecules on the compactness of the modification layer. The SEM images and the diffusion experiments of solute confirm the formation of a dense and smooth cationic modification layer. The electrodialysis experiments of the CEMs corresponding to different preparing stages with respect to H^+/Zn^{2+} system and Na^+/Mg^{2+} system show that the mono-valent perm-selectivity can be endowed successfully to the ordinary CEM. For example, the separation ability of the CEM modified by the cross-linked quaternized chitosan to protons and Zn^{2+} in solution of 2.5 g/L $ZnSO_4$ in 0.25 M H_2SO_4 increases almost 10 times. However, a remarkable increase of the electrical resistance and decrease of limiting current density is also observed after CEM modification.

Keywords: Mono-valent perm-selectivity; Cation exchange membrane; Electrodialysis; Surface modification; Chitosan

1. Introduction

It is well known that the electrodialysis technology specializes in the common desalination and concentration of electrolyte solutions by means of the alternative arrangement of ion exchange membranes. Therein, the relevant applications, such as the comprehensive utilization of sea-water, waste-water treatment, and hydrometallurgy, thirst for the cation exchange membranes with high proton leakage or selectivity to mono-valent cations [1]. At present, there are several approaches, including the selection of the membrane material [2–4], the alteration of the membrane morphology [5], and the modification of the membrane surface [6,7], to be able to adjust the affinity of the cations with the membrane or/and their migration speeds in the membrane phase. In view of the perfect properties of the current cation exchange membrane (CEM) and the

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strong maneuverability of the preparing method, the latter is often employed to prepare mono-valent perm-selective CEM. For examples, some mono-valent perm-selective CEMs are successfully prepared through the formation of a thin anion exchange layer, such as polyethyleneimine [8,9], polyaniline [10,11] and polypyrrole [12,13], on the surface of the conventional CEM by means of the coating method or the electro-deposition method. Nevertheless, the detachment of the modified layer seems to be unavoidable because its existence on the base CEM only relies on the weak electrostatic interaction. Thus, some relatively complex method for the covalent grafting of a cationic charged layer on the CEM, such as the formation of a sulfonamide bond [14] and diazonium-induced anchoring process [15], are developed.

Due to its outstanding characteristics, such as low price, rich resources, and environmental kindness, the chitosan was adopted to endow the mono-valent ion selectivity to the ordinary CEM by the electro-deposition method and coating method [16,17]. Although the feasibility was confirmed, some intrinsic problems of these conventional methods still remain unsolved. Firstly, the detachment of the polyelectrolyte layer formed by simple coating or electro-deposition method from base membrane can be observed in certain cases during long-term electrodialysis [18]. On the other hand, the existence of the strong electrostatic repulsion among the strongly charged polyelectrolyte makes against the formation of a dense modified layer during the coating or electro-deposition process. Enlightened by the preparation of the Tokuyama BP-1 bipolar membrane [19], a modified coating method is attempted in this work. That is, the base CEM will be roughened with sand paper before the coating of the chitosan solution to enhance the contacting area and possible interaction. After that, the post-quaternization of the chitosan layer is performed to endow the mono-valent perm-selectivity. Theoretically, the employment of the above-mentioned matches can be expected to tackle the above-mentioned problems to a certain extent.

2. Experimental

2.1. Materials

Chitosan is supplied by Zhejiang Jinke Biochemistry Co. Ltd., Glycidyl trimethyl ammonium chloride (GTMAC) is purchased from Shandong Guo-feng Fine Chemical Co. NaCl, $MgCl_2$, H_2SO_4, HCHO, $NaSO_4$, $ZnSO_4$, EDTA, and K_2SO_4 are analytic grade chemicals and used directly without any further purification. Indicators, EBT and XO, are newly prepared and stored at low temperature. The SELEMION CMV cation exchange membrane, the product of the Asahi Glass Co., Ltd., is chosen as the base membrane in this study. Its main properties are listed in Table 1. In addition, the specific heterogeneous anion exchange membranes (AEM, QQ-YLM_{201}) with low water osmosis and salt diffusion used in electrodialysis experiments are purchased from Zhejiang Qianqiu Environmental Protection & Water Treatment Co. Ltd., China.

2.2. The preparation of the mono-valent perm-selective cation exchange membrane

Firstly, both surfaces of the bare CEM are roughened by sand paper (3M, P2000). Then, the membrane (area: 5 cm × 5 cm) is immersed in the 2% (w/v) chitosan solution in 2% (v/v) acetic acid at room temperature for 24 h. After removed and drained the excess of chitosan solution well, the membrane is dried at 60℃ for 2h. Subsequently, the membrane is cross-linked at 60℃ for 2 h in the cross-linking solution composed of formaldehyde (7 wt.%), sodium sulfate (19 wt.%), sulfuric acid (16 wt.%), and distilled water. After rinsing with distilled water to remove excess impurities, the chitosan layer is quaternized by 25% (w/v) GTMAC at 50℃ for 12 h. In order to remove uncross-linked chitosan, the modified membrane is immersed in 2% (v/v) acetic acid for 48 h with continuously agitation. At last, the membrane is rinsed with distilled water and stored in 0.1 M sodium chloride solutions for further physio-chemical and electrochemical characterization.

2.3. Characterization

2.3.1. The diffusion of solute

When concentration difference between electrolyte solutions at both sides of an ion exchange membrane

Table 1
The main properties of the CMV commercial membrane collected from the product brochure by the company

Product name	Selemion CMV
Membrane TYPE	Cation exchange membrane
Thickness (μm)	130
Structure property	Copolymer of sulfonated styrene and divinylbenzene
Transport number of Na^+	>0.96
Backbone	Polyvinylchloride
Resistance ($\Omega\,cm^2$)	
0.5 M NaCl	3
0.5 M H_2SO_4	0.75
Burst strength (MPa)	0.4

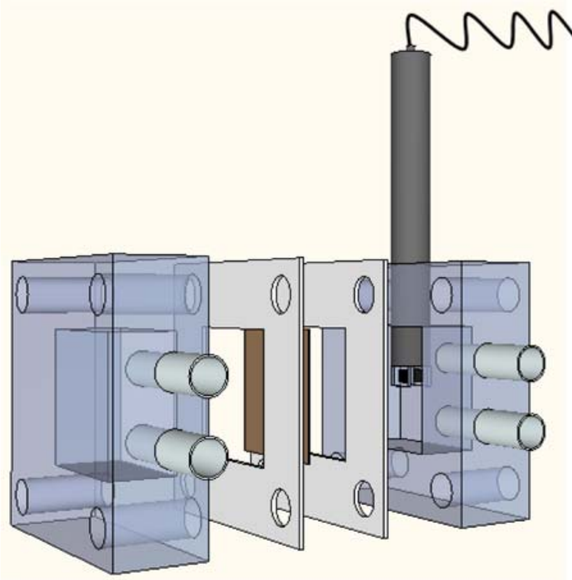

Fig. 1. The setup used for the measurement of NaCl diffusion coefficient.

is maintained, ions in a concentrating side will diffuse toward a desalting side (see Fig. 1). The ionic flux per unit time J_s can be represented by the following Fick's diffusion equation (Eq. (1)).

$$J_s = D \cdot S \cdot \frac{\Delta c}{t_m} \tag{1}$$

Here, D is the diffusion constant of salt; t_m is the thickness of membrane; D/t_m is solute permeability coefficient of salt; S is the membrane area; and Δc is the concentration difference between electrolyte solutions at both sides of an ion exchange membrane. At the beginning of the experiment, the concentrating side and desalting side are filled with 0.1 M NaCl and pure water, respectively. During the diffusion experiment, the conductivity of the desalting side is monitored in time to evaluate the quantity of the diffused salt according to the proportional relation between the conductivity and concentration in the dilute salt solution. Therefore, the permeability coefficient of salt can be described by the Eq. (2) [20].

$$\frac{D}{t_m} = \frac{V \cdot \theta}{S \Delta c_0} K \tag{2}$$

Here, V is the volume of electrolyte solution; θ is the slope of the linear relation between concentration and conductivity at the desalting side; K is the slope of the linear relation between conductivity and time at the desalting side; S is the membrane area; Δc_0 is the concentration difference between the concentrating side and desalting side.

On the other hand, the diffusion experiment of urea molecule (neutral molecule; Stokes radius: 3.3 Å) is conducted to evaluate the change in the surface compactness of the commercial CEM after the modification by the cross-linked quaternized chitosan layer. After equilibrated in aqueous urea solution (6 mg/mL) adequately, the membrane sample is clamped between the two-compartment cell in which 6 mg/mL aqueous urea solution and pure water are filled in, respectively. During the 3 h diffusion experiment at room temperature, the submersible pumps are used for the circulation of the solution in order to lessen the concentration polarization at both interfaces of membrane and solution. At last, the amount of urea permeated into the pure water side is determined with a UV–vis spectrometer (UV2450, SHIMADZU) using a 1 cm^2 quartz cell via the absorbance at 416 nm. Thus, the urea retention of the CEM can be calculated according to the following equation.

$$R = \frac{A'_C}{A_C} \times 100\% \tag{3}$$

where, A_C and A'_C is the absorbancy of urea in the concentrated compartment before and after the diffusion experiment, respectively.

2.3.2. The current–voltage measurements

In this study, a series of current–voltage curves corresponding to the different preparing stages are obtained under the same conditions using 0.2 M NaCl solution. The membrane samples are first adequately equilibrated in measurement solution for more than 48 h. After that, the investigated membrane sample and two pieces of anion exchange membranes are clamped in a home-made four-compartment cell with a four-electrode arrangement (see Fig. 2). That is, a couple of electrodes made of titanium coated with ruthenium are connected with a potentiostat/galvanostat (DF1731SD2A, Ningbo Zhongce Electronics Co., Ltd.) to supply direct current, whereas the electrical potential drop across the investigated membrane sample is measured by a couple of calomel reference electrodes. The distance between CEM surface and reference electrode is 3.5 mm. Each compartment is connected to a 250 cm^3 beaker, allowing for circulation of external solutions by a submersible pump (AP1000, Guangdong Zhenhua Electric Appliance Co., Ltd., China, with the maximal flow rate of 27 L/h). The current–voltage measurement experiments are performed by exerting a stepwise increase of the current density through the cell and recording the corresponding steady-state voltage drop values.

2.3.3. Membrane surface morphology

Scanning electron microscopy (SEM) images of the dried cation exchange membrane are recorded by S-4800 scanning electron microscopy produced by Hitachi after the gold sputter coatings on a desired membrane samples to ensure excellent conductivity.

2.3.4. Electrodialysis experiments

In order to evaluate the mono-valent perm-selectivity of the CEMs, series of electrodialysis experiments with respect to two kinds of systems, such as the H^+/Zn^{2+} system and the Na^+/Mg^{2+} system which are used to simulate the hydrometallurgy application and the seawater concentration application, respectively, are conducted using a home-made four-compartment cell similar to that for current–voltage measurements demonstrated in Fig. 2. That is, ion exchange membranes, including two pieces of anion exchange membranes and a piece of investigated cation exchange membrane (effective area, 3 cm × 3 cm), are arranged between working electrodes and separated by Plexiglas spacers (thickness, 1 cm). For the H^+/Zn^{2+} system, the electrolyte solutions, such as 200 mL of 2.5 g/L $ZnSO_4$ in 0.25 M H_2SO_4, 5 g/L $ZnSO_4$ in 0.5 M H_2SO_4, 7.5 g/L $ZnSO_4$ in 0.75 M H_2SO_4, 10 g/L $ZnSO_4$ in 1 M H_2SO_4, 12.5 g/L $ZnSO_4$ in 1.25 M H_2SO_4, are filled in dilute cell and the H_2SO_4 with the same concentration is injected into concentrated cell. For the Na^+/Mg^{2+} system, 200 mL electrolyte solution composed of 459 mMol/L Na^+ and 52.3 mMol/L Mg^{2+} is filled in dilute cell and the Na^+ (present as NaCl) with the same concentration is injected into concentrated cell [21]. The 0.5 M K_2SO_4 solution is chosen as electrode rinsing solution. Electrodialysis time is set as 80 min. The current density of 40 mA/cm^2 is exerted. The concentration of Zn^{2+} (or Mg^{2+}) is determined by EDTA complexometry titration. The value of $\%Zn^{2+}$ (or $\%Mg^{2+}$) leakage can be obtained according to the following equation:

$$\%Zn^{2+}\ \text{leakage} = \frac{\text{mass of } Zn^{2+} \text{ in concentrated cell}}{\text{mass of } Zn^{2+} \text{ in concentrated and dilute cells}} \times 100\% \tag{4}$$

3. Results and discussion

3.1. The modification of the bare CEMs

The coating method is widely adopted to prepare the mono-valent perm-selective CEMs because of its simplicity and effectiveness [7]. The fixation of the modification layer on the bare CEM depends on the electrostatic forces between them. Obviously, it is possible that the life-span of the modification layer will be shortened when facing some severe electrodialysis conditions, for examples, the frequently reversing electrodes, membrane fouling, etc. It is not difficult to understand that the roughed membrane surface is beneficial to the fixation of the oppositely charged layer due to the augmented contacting area and interaction. On the other hand, it is also easy to understand that the electrostatic repulsions among the strongly charged polyelectrolyte are unfavorable to the formation of the dense modification layer in the conventional preparing process, such as coating method and electro-deposition method.

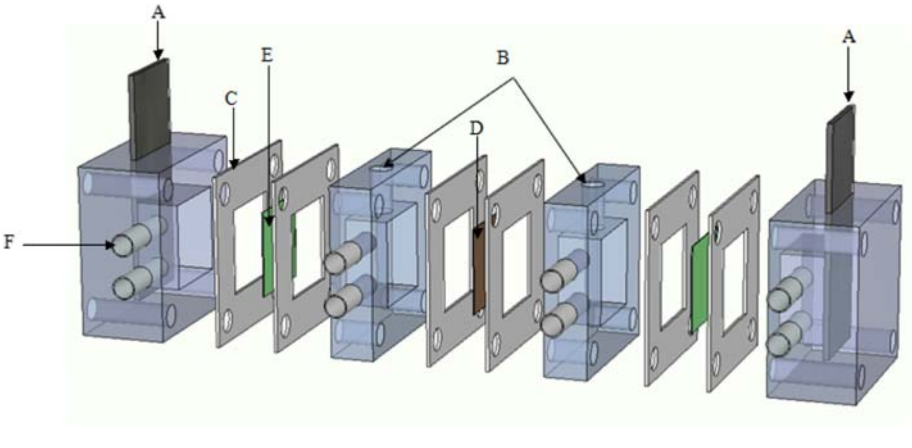

Fig. 2. Four-compartment cell configuration for current–voltage curve measurement and electrodialysis experiment. (A) working electrodes; (B) holes for calomel reference electrodes; (C) silica gel gaskets; (D) the investigated cation exchange membrane; E: anion exchange membranes; and (F) the plastic tubes used for connection with the pumps.

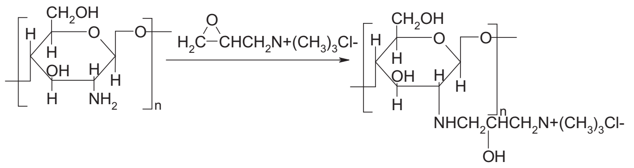

Fig. 3. The quaternized reaction between the chitosan and GTMAC.

Enlightened by the preparing method of Tokuyama BP-1 bipolar membrane, the base CEM is roughened by means of the sand paper before the coating of the chitosan solution. Obviously, this can increase the interacting points a lot, such as electrostatic interactions, H-bond interactions, van der waals interactions, etc., and even result in the formation of a interconnecting network-like structure in some local regions. Furthermore, in order to make the modification layer more durable and dense, the cross-linking process of the chitosan layer is very necessary. In this study, the cross-linking process is carried out by the simple reaction between the HCHO and amino groups of the chitosan. At last, although the weak cationic layer exists on the membrane surface resulting from the primary amine groups on the chitosan layer, its quaternization should be performed to strengthen the possible electrostatic repulsion between the CEM surface and cations. Accordingly, a post-quaternization of the cross-linked chitosan can be performed by means of the nucleophilic reaction taking placing between the remanent amine groups of cross-linked chitosan and epoxy groups of GTMAC, which is demonstrated in Fig. 3. Obviously, the formation of modified layer can be adjusted to some extent through the optimization of the relevant links in the fabrication chain such as the coating step, cross-linking step, quaternization step, and so on.

3.2. The alteration of the surface morphology during the membrane preparation

In Fig. 4, the alteration process of surface morphology during the membrane preparation is recorded. Compared with the smooth surface of the bare CEM shown in Fig. 4(A), we can see clearly from Fig. 4(B) that the membrane surface has been roughened with the sand paper. Fig. 4(C) displays the surface morphology of the CEM treated by a series of the surface modification steps, including roughening, coating, cross-linking and the subsequent quaternization. It

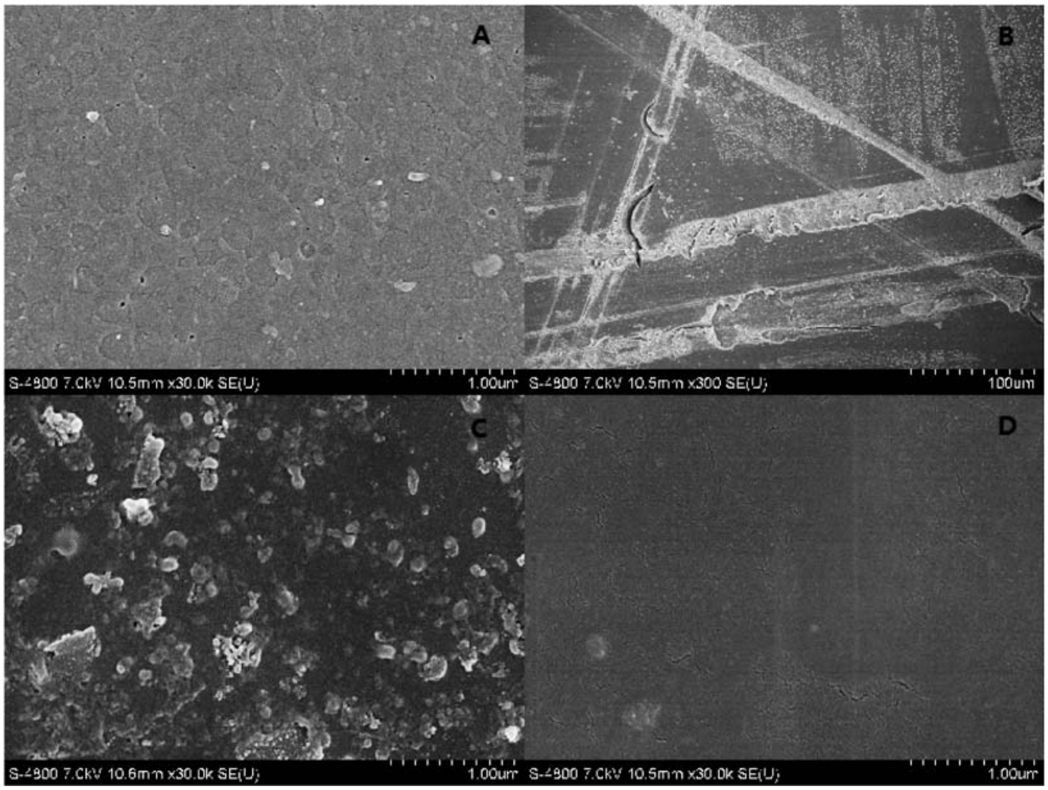

Fig. 4. SEM images for: (A) the bare CEM; (B) the surface-roughening CEM; (C) the modified CEM without surface-cleaning; and (D) the modified CEM after washing thoroughly with 2% (v/v) acetic acid.

can be seen that there are substantive blocky particles existing on the membrane surface, which should be ascribed to the agglomeration of the chitosan. After that, the membrane surface is washed thoroughly with the 2% (v/v) acetic acid to remove the uncross-linked chitosan. As a comparison, it can be seen from the Fig. 4(D) that the blocky particles mentioned above disappear. It is worth noting that, the surface of the modified CEM seems more tight and smooth than that of the bare membrane. Of course, this also proves the formation of the modification layer and the existence of a good adhesion between the chitosan layer and the membrane surface.

3.3. The diffusion experiments of solute

It can be seen from Fig. 5 that the diffusion coefficient of NaCl for the CEMs increases to some extent along with the introduction of different modification steps, especially after the formation of cross-linked quaternized chitosan layer on the CEM surface. Although the electrostatic repulsion forces between the membrane surface and Na^+ should increase after modification, the diffusion of NaCl through membrane is aggravated. This should be attributed to the permeation of Cl^- facilitated by the cationic charged layer. Generally speaking, it is easier for anions to approach membrane surface due to their relatively small volume when no electric field is exerted. After the introduction of the cationic layer, the more Cl^- will move towards membrane surface driven by electrostatic attraction force. So, Cl^- will accumulate membrane surface and its concentration increases. Obviously, this will facilitate the diffusion of Cl^- through membrane. For the sake of electrical neutrality, the diffusion of Na^+ is strengthened indirectly. Because the electrical interactions among the charged particles are proportional to quantity of electricity and inversely propotional to the square of the distance, the results demonstrated in Fig. 5 reflect that the positive charge density increases after modification, especially the cross-linking and/or quaternization treatment.

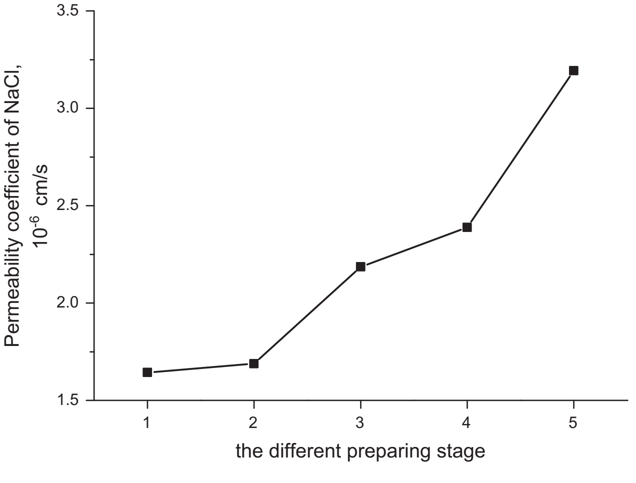

Fig. 5. The permeability coefficient of NaCl for the CEMs corresponding to the different preparing stage. 1. The bare CEM; 2. The surface-roughening CEM; 3. The CEM modified by cross-linked chitosan; 4. The CEM modified by quaternized chitosan; and 5. The CEM modified by cross-linked quaternized chitosan.

On the other hand, the diffusion experiments of the urea, the neutral molecule, show that the urea molecules retention of the CEM modified by cross-linked quaternized chitosan increases by 4.09%. Obviously, this indicates that the surface of the CEM become denser after modification.

3.4. The current–voltage curves

It is well known that under a certain current density, concentration polarization will gradually develop in electrolyte solution adjacent to the membrane due to the difference in ion transport numbers within the membrane and solution. According to the classical theory of concentration polarization, currents larger than the limiting current density should not be expected. As one of important researching tools in this field, the current–voltage curve is usually employed, for example, to explore the origin of the over-limiting current [22–24]. Generally, a typical current–voltage curve should embrace three characteristic regions. First, a linear part is called as ohmic region, which denotes the ohmic resistance faced by ionic transport. Second, a plateau (or a pseudo-plateau) is called as the current–limiting region, which gives some information on the diffusion boundary layer. Third, another linear part of current–voltage is called as electro-convection region. It is worthy of noting that a lot of investigations have shown the experimental conditions remarkably influence the shape of current–voltage curve, for examples, hydraulic environment and the distance between the membrane surface and reference electrode [25]. Therefore, in this study, the same measurement conditions are adopted in order to grasp the relative change trend of ohmic resistance and limiting current density after the relevant modification step is performed, such as roughening, coating, cross-linking, and quaternization.

Fig. 6 demonstrates a series of current–voltage curves corresponding to different preparing stages. First, the ohmic resistance can be calculated according to the slope of curve in the ohmic region. Compared with the bare CEM, it can be seen that (1) the ohmic resistance of the surface-roughening CEM reduces a little. This should be related to the decrease of membrane thickness after surface roughening; (2) the ohmic resistance of the modified CEM by chitosan increases by 10%. In addition, the increasing amplitude for modified CEMs after quaternization seems to be much higher. This phenomenon agrees well with the results reported in the literature [25]. Obviously, this should be attributed to the existence of modification layer which resists the ionic transport to a certain extent. Moreover, the electrostatic repulsion between the modification layer and cations become larger after quaternization of the chitosan layer.

In addition, it can be also observed from Fig. 6 that the current–voltage curve of CEM treated by surface-roughening or chitosan coating display similar shape to that of the bare CEM in the investigating range. That is, only the ohmic region is observed. However, for CEM modified by quaternized chitosan whether it is cross-linked or not, a plateau (or a pseudo-plateau) region and even electro-convection region are observed. This indicates that the presence of the quaternized chitosan layer on the surface of CEM hinder the ionic transport to a large extent. The depletion of salt ions on the dilute side of CEM appears earlier. Hence, the limiting current density of the modified CEM is decreased.

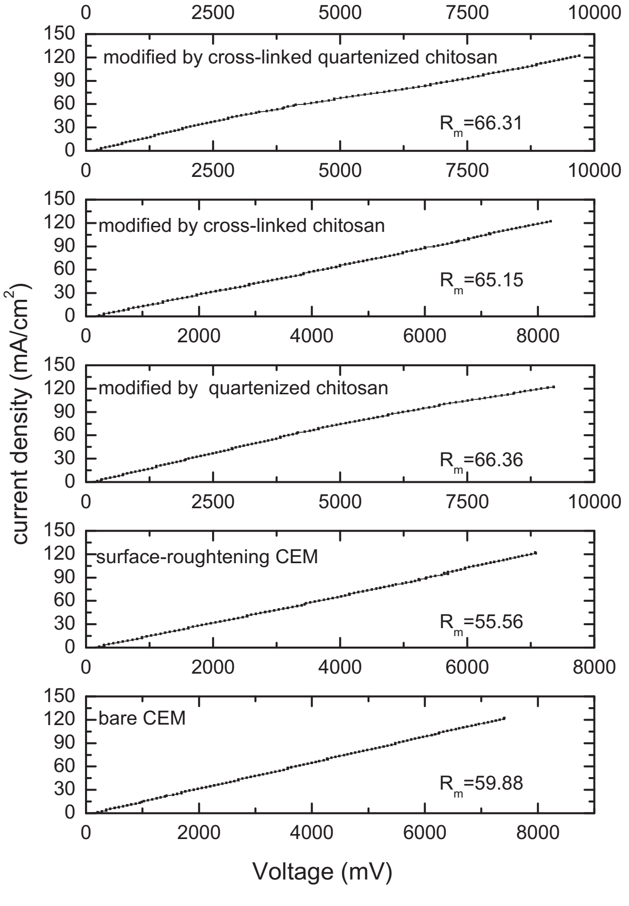

Fig. 6. The series of current–voltage curves corresponding to different preparing stage (R_m, membrane electrical resistance, $\Omega\,cm^2$).

Indeed, the common problems, such as increase of electrical resistance and decrease of limiting current density, are often encountered in the preparation of mono-valent permselectivity CEM. For example, Chapotot et al. modified the CRA membrane with a layer of polyethyleneimine and observed a remarkable increase of the electrical resistance (about 50%) in contact with $HCl/CaCl_2$ mixed solution [26]. In addition, Chamoulaud et al. modified the CMX membrane by formation of a sulfonamide bond for separation of protons and metallic cations. The experimental results showed the limiting current density of the modified CEM in HCl reduced from $9.6\,mA/cm^2$ to $3\,mA/cm^2$ (about 69%) [25]. It is well known that the membrane electrical resistance is the main reason for the energy consumption of the electrodialysis process. On the other hand, a relatively high limiting current density is also expected in order to make the electrodialysis work under high current density. Accordingly, how to further reduce the electrical resistance and increase the limiting current density of the modified membrane still leaves an immense space for the subsequent development of the membrane preparing method.

3.5. Electrodialysis experiments

In order to clarify the effects of the different modification steps on the mono-valent selectivity of CEMs, the experiments—in which the leakage of the multivalent ions is investigated—are conducted and displayed in Fig. 7. Just as narrated in introduction section, the mono-valent selective CEMs are badly needed in the fields such as the hydrometallurgy and seawater concentration. Accordingly, H^+/Zn^{2+} system and Na^+/Mg^{2+} system are employed to simulate the above-mentioned applications, respectively. For H^+/Zn^{2+} system, it can be seen from Fig. 7 that (1) As a kind of physical treatment, the surface-roughening step almost has no influence on the mono-valent perm-selectivity of CEM; (2) Just as expected, the quaternization of chitosan may augment the electrostatic repulsion force between the cations and CEM surface and strengthen the mono-valent perm-selectivity; (3) besides contributing to the adherence of modified layer on CEM, the cross-linking step can effectively increase the mono-valent perm-selectivity. This may be attributed to the augmentation of the pore-sieving effect and electrical repulsion effect due

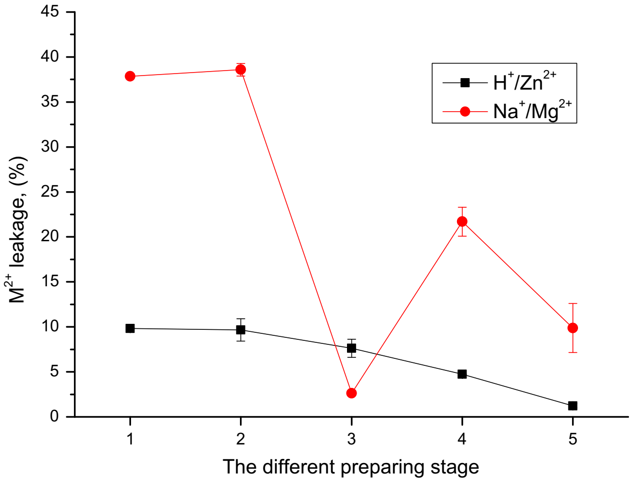

Fig. 7. The leakage of Zn^{2+} and Mg^{2+} for the CEMs corresponding to the different preparing stage. 1. The bare CEM; 2. The surface-roughening CEM; 3. The CEM modified by cross-linked chitosan; 4. The CEM modified by quaternized chitosan; and 5. The CEM modified by cross-linked quaternized chitosan. The composition of H^+/Zn^{2+} system: 7.5 g/L $ZnSO_4$ in 0.75 M H_2SO_4; the composition of Na^+/Mg^{2+} system similar to seawater [21]: 0.459 M Na^+ and 0.0523 M Mg^{2+}. The current density: 40 mA/cm^2. The electrodialysis time: 80 min.

to the increase of the compactness of modification layer. For Na^+/Mg^{2+} system, the CEMs modified by chitosan and quaternized chitosan also embrace outstanding mono-valent perm-selectivity. However, different from the case for the H^+/Zn^{2+} system, the CEM modified by cross-linked chitosan display the lowest leakage of Mg^{2+}. This disagrees with the presupposition and needs further study. Anyway, the experimental results show the selective separation behavior of the mono-valent perm-selective CEMs should be related to the composition of the electrolyte solution.

Furthermore, H^+/Zn^{2+} system is taken as example to evaluate the effect of electrolyte solution composition on the separation behavior of the modified CEM between protons and metallic cations. According to Fig. 8, it can be seen that, for 10 g/L $ZnSO_4$ in 1 M H_2SO_4 and 12.5 g/L $ZnSO_4$ in 1.25 M H_2SO_4, the Zn^{2+} leakage of the modified CEM almost equals to 0 and that of the bare CEM is only about 5%. It indicates that the separation between protons and metallic cations is an easy job for electrolyte solution having high content of protons. Obviously, this mainly results from the distinct difference between their transport numbers, for examples, the transport number of H^+ and Zn^{2+} in 0.05 mol/L solution is 0.8292 and 0.397 [27], respectively. However, for solution of 2.5 g/L $ZnSO_4$ in 0.25 M H_2SO_4, the Zn^{2+} leakage of the bare membrane is as high as 43.2%. This shows it is difficult to separate protons from metallic cations in solution with low content of protons. Fortunately, the Zn^{2+} leakage of the modified membrane is only 4.45% for the above-mentioned system. The experimental results confirm that it is the electrostatic repulsion barrier between the protonated amine/imine groups existing on the chitosan chain and cations results in the reduction of the penetration of divalent cations with respect to protons.

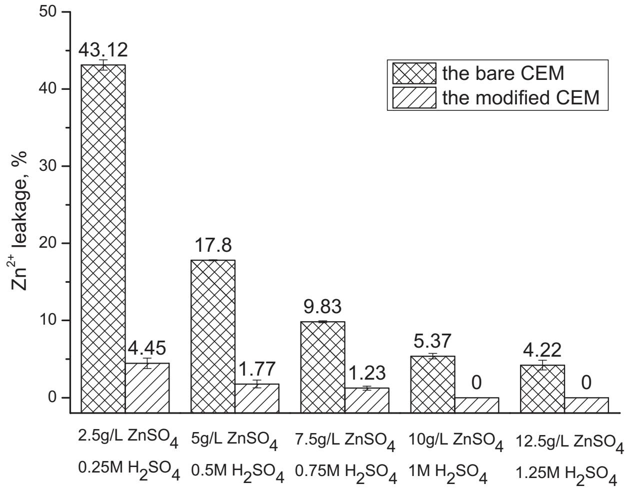

Fig. 8. The leakage of Zn^{2+} for the different electrodialysis systems under 40 mA/cm^2.

4. Conclusions

In this work, a modified coating method for preparing the mono-valent perm-selectivity CEM is attempted. That is, a surface-roughening step is introduced before the conventional coating process to strengthen the interaction between the modification layer and the bare membrane due to the increase of the contacting area. Furthermore, the post-quaternization of the chitosan layer is carried out in order to weaken the possible effect of the electrostatic repulsion among the cationic charged macromolecules on the compactness of the modification layer. The SEM images and the diffusion experiments of solutes also confirm the formation of the dense and smooth cationic modification layer. The electrodialysis experiments of H^+/Zn^{2+} system and Na^+/Mg^{2+} system show that mono-valent perm-selectivity is endowed successfully to the ordinary CEM after the fixation of the chitosan layer and quaternized chitosan layer. For example, the separation ability of the CEM to protons and Zn^{2+} in solution of 2.5 g/L $ZnSO_4$ in 0.25 M H_2SO_4 increases almost 10 times after modification according to the method put forward in this work. On the other hand, the electrodialysis experiments with respect to Na^+/Mg^{2+} system and H^+/Zn^{2+} system with different concentration show the mono-valent perm-selectivity of CEM is closely related to the system composition such as concentration and ion species. Moreover, the experiments of CEMs corresponding to the different preparing stage show that the cross-linking step can increase the compactness of modification layer and effectively increase the mono-valent permselectivity besides contributing to the adherence of modified layer on the original CEM. However, a relatively remarkable increase of the membrane electrical resistance and decrease of limiting current density resulting from the introduction of the modification layer is still observed. That is to say, there is still much work to be done for improving the preparing method.

Acknowledgments

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