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Influence of the ratio of resin to polymeric binder on the heterogeneity of cation-exchange membranes

Sang-Don Han[a,1], Hong-Joo Lee[b,*], Seung-Hyeon Moon[a]

[a] *School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheomdangwagi-ro, Buk-gu, Gwangju 500-712, South Korea, Tel. +82 62 970 2476; Fax: +82 62 970 2434; email: sdhan79@gmail.com (S.-D. Han), Tel. +82 62 970 2435; Fax: +82 62 970 2434; email: shmoon@gist.ac.kr (S.-H. Moon)*
[b] *Department of Bioenergy Science and Technology, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, South Korea, Tel. +82 62 530 2040; Fax: +82 62 530 2047; email: hjlee68@jnu.ac.kr*

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ABSTRACT

In this study, heterogeneous cation-exchange membranes were prepared by a casting method using mixtures of cation exchange resin and polymeric binder for the application of desalination and water treatment. The influence of the ratio of cation-exchange resin to polymeric binder on the electrochemical properties, such as the characteristic values in the current–voltage relationship, electrical conductivity, and chronopotentiometric values, was investigated and the preparation method was optimized based on the characterized properties of the heterogeneous cation-exchange membranes. The heterogeneity, determined by their ion-exchange resin content, was estimated based on the characterized electrochemical properties, which is related to the inter-gel phase fraction and the conducting phase. It was observed that the heterogeneity of the prepared cation-exchange membranes increased with transition time and limiting current density. In electrodialytic experiments, the heterogeneous cation-exchange membranes showed reasonably good desalination performance compared to commercial heterogeneous membranes, which is related to the heterogeneity as well as the membrane properties.

Keywords: Cation-exchange membrane; Desalination; Electrochemical properties; Electrodialysis; Heterogeneity

1. Introduction

Ion-exchange membranes have applications in various areas, such as electrodialysis (ED), diffusion dialysis, electrodeionization, membrane electrolysis, fuel cells, storage batteries, electrochemical synthesis, and others. ED employs ion-exchange membranes with charged functional groups and is used to remove ions from an electrolyte solution or to concentrate solutions in an electric field [1]. To increase desalination performance in electrodialysis process, it is important to develop ion-exchange membranes with low electrical

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*Corresponding author.

[1] Present address: Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA, Tel. +1 630 252 1035; Fax: +1 630 972 4535.

resistance, high ion permselectivity, good mechanical strength, chemical stability, and durability [2,3].

Compared to homogeneous membranes, heterogeneous ion-exchange membranes, which can be prepared with simple method at very low cost, have several advantages, such as good mechanical properties and dimensional stability [4]. To obtain superior ion-exchange membranes, the following methods have been considered: variation of functional groups, selection of polymeric matrices, use of fillers, nanoparticles, and surfactants, modification of membrane structures by plasma methods, and polymer coatings [5,6].

An ion-exchange membrane has a heterogeneous structure consisting of a gel phase and an inter-gel phase [7–9]. The gel phase has a relatively uniform distribution of functional groups and hydrophilic parts of the matrix polymer chains, whereas the inter-gel refers to the interstices between the elements of the gel phase filled with an electroneutral solution [10–14]. It is known that heterogeneous structures affect the electrochemical behavior of ion-exchange membranes, such as properties related to concentration polarization, membrane conductance, ion selectivity, and ion transport number. In addition, the heterogeneous structures can affect limiting current density, transition time, etc. [15–18].

It is necessary to consider the process performance, which depends on the heterogeneity of ion-exchange membranes in order to assess the technical viability of the ED process [19–21]. In a previous study, the degree of the heterogeneity of ion-exchange membranes was estimated using a heterogeneous model based on the electrochemical properties of commercial anion-exchange membranes employing three monovalent organic acids and an inorganic electrolyte (NaCl) [18]. However, the influence of the heterogeneity on the desalination process was not studied, and, therefore, the feasibility of the ion-exchange membrane application was not assessed in the previous report.

In the present study, heterogeneous cation-exchange membranes were prepared by a casting method by dispersing ion exchange resin particles in a film-forming binder solution. The influence of the heterogeneity of cation-exchange membranes, determined by their ion-exchange resin content, on the electrochemical properties, such as electrical conductivity, chronopotentiometric values, and characteristic values in the current–voltage relationship, was investigated. In addition, electrodialytic experiments were performed using the prepared heterogeneous cation-exchange membranes for the applications of the desalination and water treatment.

2. Materials and methods

2.1. Preparation of heterogeneous cation-exchange membranes

In this study, the heterogeneity was controlled by the resin content in the heterogeneous cation-exchange membrane structure, i.e. the ratio of cation-exchange resin to polymeric binder. Heterogeneous cation-exchange membranes were prepared by mixing a cation-exchange resin, Amberlite IR120 Na (Rohm & Haas Co., Esslingen, Germany), with a polymeric binder, polyvinyl butyral (PVB) (Sigma, St. Louis, MO, USA). The molecular structure of PVB contains hydroxyl groups and alkyl groups; the former groups represent the hydrophilic groups and the latter groups improve hydrophobicity [22]. Polyethylene glycol (PEG) (Sigma) and a mixture of toluene (Fisher Scientific Inc., Pittsburgh, PA, USA) and ethanol (Merck, Darmstadt, Germany) were used as a modifier and a solvent, respectively.

The heterogeneous cation-exchange membranes were prepared by the casting method; i.e. the dispersion of ion-exchange resin particles followed by evaporation of the solvent and lamination on a glass plate. After cation-exchange resin particles were powdered using a ball mill, a slurry of resin powder with PVB was prepared in a mixture of solvents (toluene and methanol) and the modifier. The amount of the modifier was set to 10% of the total amount of the mixture of the cation-exchange resin and polymeric binder. The slurry was then cast onto a silica-coated film using a tape casting machine, STC-14AM (Hansung Systems Inc., Seoul, Korea) with a controllable doctor blade. After drying for 2 h, the film was laminated with a hot press at 1,000 psi and 90˚C for 15 min. The prepared cation-exchange membranes were then conditioned by equilibrating them in 1.0 M HCl solution at 40˚C for 1 h. Table 1 shows the different compositions for the preparation of heterogeneous cation-exchange membranes.

2.2. Characterization of the physicochemical and mechanical properties

The surface and cross-sectional morphologies of the prepared membranes were examined by field emission scanning electron microscopy (FE-SEM) (S-4700, Hitachi, Tokyo, Japan). An energy dispersive X-ray (EDX) analysis was conducted with FE-SEM for the compositional analysis. All membrane samples were dried for 24 h in a vacuum oven prior to analysis.

The physical and chemical properties of the prepared cation-exchange membranes, such as transport

Table 1
Preparation methods for preparing the heterogeneous cation-exchange membranes

Membrane[a]	Cation exchange resin (IR120 Na) (%)	Polymeric binder (polyvinyl butyral) (%)
HCM-10	10	90
HCM-20	20	80
HCM-30	30	70
HCM-40	40	60
HCM-50	50	50
HCM-60[b]	60	40

[a] The amount of the modifier (polyethylene glycol) was set to 10% of total amount of cation-exchange resin and polymeric binder for all membranes.

[b] Cation-exchange membrane could not be prepared at the ratio of 70% (resin) and 30% (polymeric binder).

number, electrical resistance, ion exchange capacity, and water content, were characterized using methods described elsewhere [18,23].

The transport number of the counter-ion through cation-exchange membranes was measured by the membrane potential using Ag/AgCl electrodes in a system of 0.1 M/0.5 M NaCl. The electrical resistance of the cation-exchange membranes was measured in a 0.5 M NaCl solution at a fixed frequency of 100 kHz using a clip cell connected to an LCZ meter (Model 2321, NF Electronics, Tokyo, Japan). Ion-exchange capacity, expressed as meq/g-dried membrane, was estimated after the membranes were soaked for 24 h in 0.1 M HCl solution. The water content of the membranes was determined by measuring the membrane weight difference between the wet and dried state after equilibrated with an electrolyte solution.

A universal test machine, Instron 5567 (Instron Corp.), was used to measure the mechanical properties of the cation-exchange membranes under the conditions of 100 mm span and 0.5 mm/min cross-head speed.

In the study, the characterized values of the prepared heterogeneous cation-exchange membranes were compared with those of the commercial cation-exchange membranes, MC3470 (Sybron Chemicals Inc., Birmingham, NJ, USA), LinanC (Linan Euro-China Co., Shanghai, China), and the homogeneous cation exchange membrane, CMX (Astom, Tokyo, Japan).

2.3. Characterization of the electrochemical properties

The chronopotentiometric analysis was conducted in 0.025 M electrolyte solution using a two-compartment cell with a membrane effective area of 0.785 cm^2. A constant current was supplied by a potentiostat/galvanostat, PGSTAT 30 (Electrochimie, Eidenhoven, The Netherlands) and the potential was measured between reference electrodes (Ag/AgCl) near the membrane–solution interface [24].

The current–voltage curves for the membranes were obtained in the same cell used in the chronopotentiometric analysis. The electrical current was supplied by the potentiostat/galvanostat connected to a pair of Ag/AgCl electrodes at the current scanning rate of 1.0 μA/s. The potential difference across the cation exchange membrane was measured using two Ag/AgCl electrodes immersed in Luggin capillaries.

In addition, the specific conductivities of the membranes were measured in NaCl solution at concentrations of 5–100 mM for the relationship between the heterogeneity and conductance. The conductivity of electrolyte and examined membrane was estimated by respective area electrical resistance. The area resistance was measured from the difference between the sum of area resistance with the solution and membrane and the area resistance for the solution alone. Based on the electrical resistance measurements, the membrane conductance, κ^m, was calculated by using membrane area and thickness [18]. All experiments were conducted at 25˚C.

2.4. Process performance in electrodialytic experiments

A unit cell pair of ED stack, having a total effective area of 40 cm^2, was used for desalination experiments with different cation-exchange membranes and a common anion exchange membrane, AMX (Astom, Japan). Five hundred milliliter of 0.05 M NaCl was circulated through the compartment at a flow rate of 100 mL/min using a peristaltic pump. An initial concentrate of 500 mL of 0.025 M of NaCl was circulated at a flow rate of 100 mL/min. For all electrodialytic experiments, 500 mL of 3% Na_2SO_4 was circulated in the electrode rinse compartments. Electrical current was supplied by a power supply (Agilent 6654A, Palo Alto, CA, USA) during experiments.

The pH and conductivities of the dilute and concentrate solutions were measured by an Orion 250A pH meter (Thermo Fisher Scientific Inc., Rockford, IL, USA) and a WD-35631 conductivity meter (Oakton Instruments, Vernon Hills, IL, USA), respectively. The voltage drop over the membranes was measured using a digital multimeter, CD721 (Sanwa Electric Instrument Co., Tokyo, Japan).

3. Results and discussion

3.1. Physicochemical and mechanical properties of the prepared heterogeneous membranes

Microscopic structures in the surface and cross-sectional morphologies of the heterogeneous membranes were observed using FE-SEM. In the analysis of elemental composition using SEM-EDX, sulfur, oxygen, and sodium were found in the prepared heterogeneous cation exchange membranes, suggesting that the membranes have sulfonic ($R\text{-}SO_3^-$) groups.

The influence of cation-exchange resin on the physicochemical and mechanical properties of the membranes was investigated by varying the ratio of resin to polymeric binder. The characteristic properties of the prepared membranes are shown in Table 2. As the amount of the resin increased, water content and ion exchange capacity of prepared membranes increased mainly due to the high resin content in the membrane structure. The transport numbers of the prepared membranes increased as the resin content increased to 40%, and remained almost constant even at the higher resin content than 40%. The electrical resistance of the membranes decreased with increasing resin content, as shown in Table 2.

In the case of the mechanical properties, the measured values of the prepared membrane modulus were similar for all prepared membranes as 0.12–0.16 MPa. Among heterogenous cation membranes, HCM-10 showed the highest mechanical strength due to higher amount of the polymeric binder.

The characteristic properties of cation-exchange membranes were compared with those of commercially available heterogeneous membranes, i.e. two heterogeneous membranes, (MC3470 and LinanC) and the homogeneous membrane (CMX), as shown in Table 2. Among commercial membranes, MC3470 showed significantly high modulus value of 0.67 MPa. As shown in Table 2, the heterogeneous membranes with resin content higher than 40% showed reasonably good properties compared with commercially available membranes.

3.2. Electrochemical properties and heterogeneity of the prepared heterogeneous membranes

3.2.1. Relationship between heterogeneity and the chronopotentiometric values

A constant current was supplied by a potentiostat/galvanostat and the potential was measured using a reference electrode (Ag/AgCl) for the characterization of the chronopotentiometric properties. The chronopotentiometric curves at various current densities (3.0–6.0 mA/cm^2) are shown in Fig. 1. Measurements of the transition time, τ, gave a value of 12.5 s for HCM-40, which is similar value with MC3470 and LinanC. The value of HCM-40 was lower than homogeneous cation-exchange membrane, CMX (19.5 s). A lower value of τ indicates a faster depletion of ions near the heterogeneous membranes due to reduced ion-permeable area [18]. The reduced ion-permeable area in the structures of heterogeneous membranes results in

Table 2
Physicochemical and mechanical properties of prepared cation-exchange membranes

Mem	Thickness (μm)	Water content (%)	IEC (meq/g)	Transport number	Electrical resistance (Ω cm^2)	Modulus (MPa)
HCM-10	270	26	0.6	0.75	339.7 ± 13.4	0.27
HCM-20	290	30	1.1	0.87	137.2 ± 1.3	0.16
HCM-30	330	50	1.7	0.88	40.5 ± 1.8	0.14
HCM-40	360	59	2.3	0.91	15.2 ± 0.1	0.12
HCM-50	370	64	2.6	0.91	7.2 ± 0.2	0.12
HCM-60	470	73	3.1	0.90	5.2 ± 0.1	0.14
MC3470[a]	410	19	1.7	0.92	17.6 ± 0.1	0.67
LinanC[a]	420	67	2.5	0.91	15.7 ± 0.2	0.16
CMX[b]	170	24	1.6	0.96	3.2 ± 0.1	0.14

[a] Commercially available heterogeneous cation-exchange membrane.

[b] Commercially available homogeneous cation-exchange membrane.

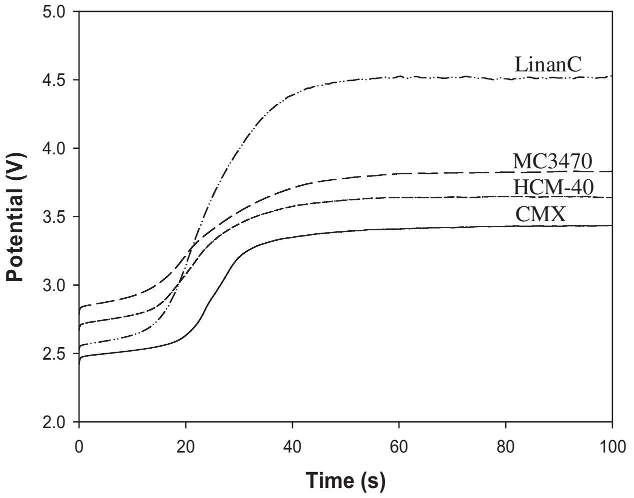


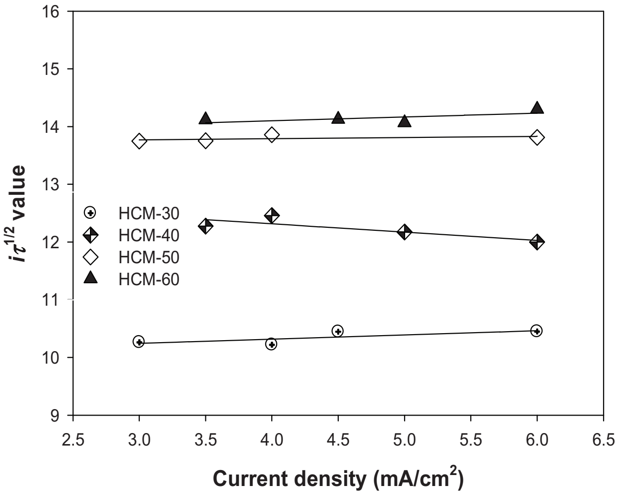
Fig. 1. Chronopotentiometric curves for cation-exchange membranes (current density of 3.5 mA/cm^2).

localized current with higher current density in the conductive region of the ion-exchange membrane [23].

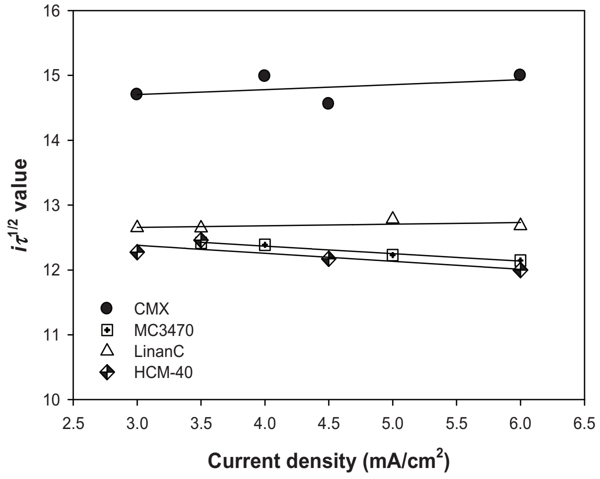
Fig. 2 compares the values of $i\tau^{1/2}$ at various current densities in the prepared heterogeneous and commercial cation exchange membranes. As shown in the figure, $i\tau^{1/2}$ decreased with increasing current density when the current density was low. And the values were constant at high current densities, which are related to natural convection at the diffusion boundary [24]. As shown in Fig. 2(a), the values of $i\tau^{1/2}$ increased for HCM-30 to HCM-60 as the amount of ion-exchange resin, or the ion-permeable region, increased. The electrochemical properties of HCM-10 and HCM-20 could not be characterized because of their small effective areas. Fig. 2(b) shows the average $i\tau^{1/2}$ values for commercial membranes and the HCM-40 membrane. It is evident that HCM-40 membrane showed similar value with MC3470 and LinanC and that the homogeneous CMX showed highest value of $i\tau^{1/2}$. The chronopotentiometric results are summarized in Table 3.

In this study, quantitative fractions of the conducting regions were obtained using the modified Sand equation based on the heterogeneous model [25]. Using the transport number of a counter-ion through the membrane structure, the conductive phase fraction of an ion-exchange membrane (ε) was estimated with the following equation:

$$\varepsilon = \frac{2i\tau^{1/2}(t_m - t_\pm)}{C_0 zF(\pi D)^{1/2}} \tag{1}$$



(a) Prepared heterogeneous cation membranes



(b) Commercial cation exchange membranes with HCM-40

Fig. 2. $i\tau^{1/2}$ values of the cation-exchange membranes as a function of current density.

where i is current density, τ is the transition time determined by the chronopotentiometric measurements, and t_m and $t_\pm$ are the transport numbers of the counter-ion in the membrane and solution phase, respectively. In addition, D is the diffusion coefficient of the electrolyte in solution, F is the Faraday constant, C_0 is the solution concentration, and z is the charge valence, respectively. The diffusion coefficient of NaCl (1.61×10^{-5} cm^2/s) and the transport number of Na$^+$ in the solution phase were obtained from the literature [25].

Table 3 shows the values of ε calculated with Eq. (1) for the prepared and commercial cation-exchange membranes. In the table, the fractional conducting regions of the prepared membranes increased with

Table 3
Characteristic values of the chronopotentiometry of cation-exchange membranes

Membrane[a]	Transition time (τ) @3.5 mA/cm^2 (s)	$i\tau^{1/2}$ (mA/cm^{2}s$^{1/2}$)	Fraction of conducting phase (ε)
HCM-30	9.6	10.4	0.58
HCM-40	12.5	12.2	0.73
HCM-50	15.0	13.7	0.82
HCM-60	17.2	14.1	0.83
MC3470	12.7	12.4	0.76
LinanC	13.2	12.7	0.76
CMX	19.5	14.8	0.98

[a] HCM-10 and HCM-20 membranes were not suitable for the characterization of electrochemical properties because only small area was available.

increasing ion-exchange resin content due to the presence of more charged functional groups on the prepared membrane structure. In addition, the fraction of the conducting region in the homogeneous membrane had a relatively high value compared to those of the heterogeneous membranes, as expected [21]. As shown in Table 3, the values of ε increased as the resin content was increased in the heterogeneous membrane structures. The ε values of commercial heterogeneous membranes, MC3470 and Linan C, were estimated to be same as 0.76, while that of the homogeneous membrane, CMX, was higher, indicating larger conducting regions in the membrane structure, as expected [24].

3.2.2. Relationship between heterogeneity and membrane conductance

The specific conductivities of the membranes were measured in different concentrations of NaCl solution to investigate the relationship between heterogeneity and membrane conductance. As shown in Fig. 3, membrane conductance initially increased as the NaCl concentration increased, and then remained steady even at higher electrolyte concentrations. For all solution concentrations, membrane conductance increased with increasing resin content. An increase in the ion-exchange resin content resulted in higher membrane conductivity since ion-exchange resins have functional groups acting as conducting sites.

According to the Zabolotsky's model, the isoconductance of membrane, κ^m_{iso}, can be determined at the intersection point of two lines between conductance (κ^m and κ_s) and electrolyte concentration [24]. Hence, the conductance of the joint gel phases for different membranes, κ_g, can be also evaluated at the isoconductance point; i.e. $\kappa^m_{\text{iso}} = \kappa_s = \kappa_g$.

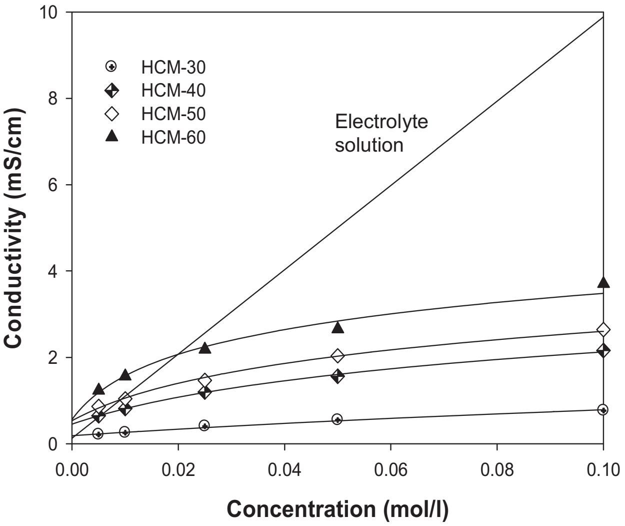
Table 4 shows the isoconductance values and the corresponding isoconcentrations of the heterogeneous and commercial cation-exchange membranes. The isoconductance of the heterogeneous membranes increased as the amount of resin in the membrane structure increased. The value of κ^m_{iso} for the homogeneous membrane was much higher than those for the heterogeneous membranes, which is related to high exchange capacity.

Values of the volume fraction of the interstitial phase, f_2, were evaluated from the slope of the graphs of ln k^m vs. ln k_s, according to Eq. (2), and the resulting values were listed in the fourth column of Table 4:

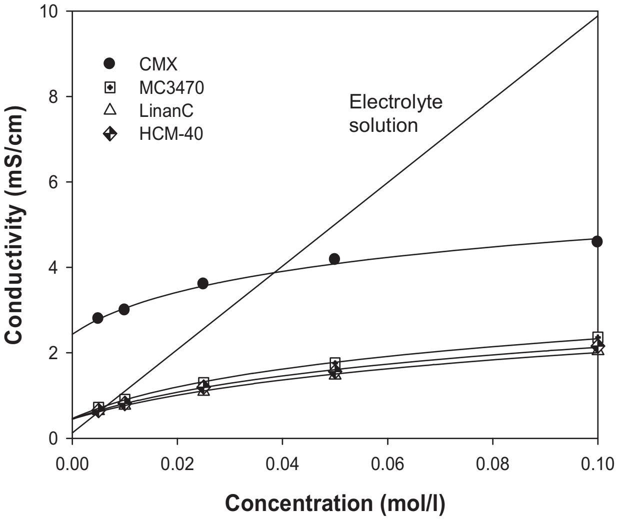
$$\ln k^m = f_1 \ln k_g + f_2 \ln k_s \qquad (2)$$

where k^m, k_g, and k_s are the conductivity of the membrane, inter-gel phase, and the electrolyte solution, respectively. In addition, f_1 is the volume fraction of the joint-gel phase in the active region and f_2 is the volume fraction of the inter-gel phase in the membrane structure. As indicated in Eq. (2), the f_2 value can be estimated by the linear relationship between ln k^m and ln k_s, as shown in Fig. 4. The f_2 values decreased as the amount of resin in the prepared heterogeneous membranes increased. The f_2 values of MC3470 and LinanC were estimated to be 0.45 and 0.44, respectively. Meanwhile, the value of the homogeneous CMX membrane was estimated to be 0.20, which is similar to that determined in previous studies [21,24].

The conductivities for the heterogeneous cation-exchange membranes were lower than those of homogeneous membranes (Fig. 4). These lower values are related to the low conducting region fraction, or high fraction of interstitial phases, in the heterogeneous membrane structure [24]. In the heterogeneous model, an ion-exchange membrane consists of a non-conducting (inert) phase, a gel phase, and an interstitial phase; thus, heterogeneous membranes showed low conductivity values compared to homogenous membranes due to the larger area of the non-conducting phase [25].

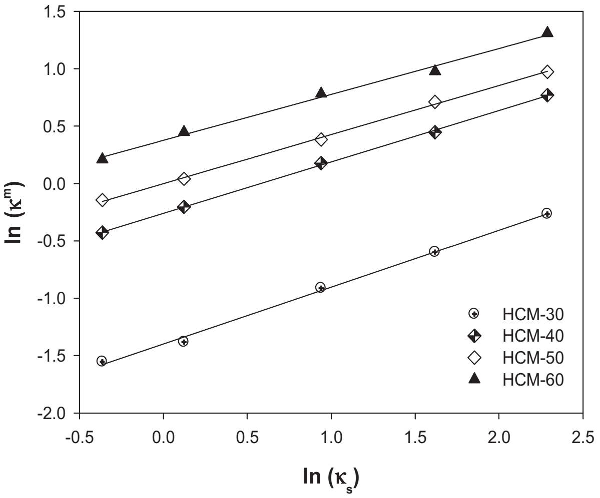


(a) Prepared heterogeneous cation exchange membranes

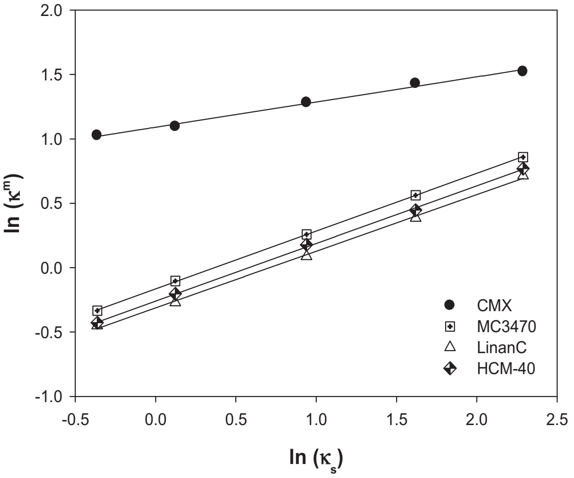


(b) Commercial cation exchange membranes and HCM-40

Fig. 3. Conductivities of cation-exchange membranes and NaCl concentration.



(a) Prepared heterogeneous cation exchange membranes

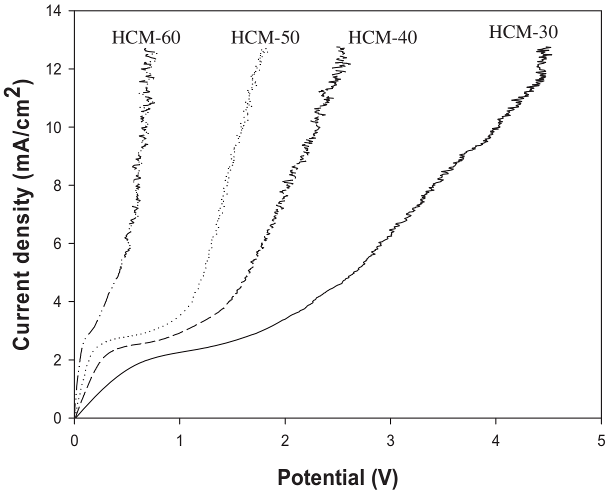


(b) Commercial cation exchange membranes with HCM-40

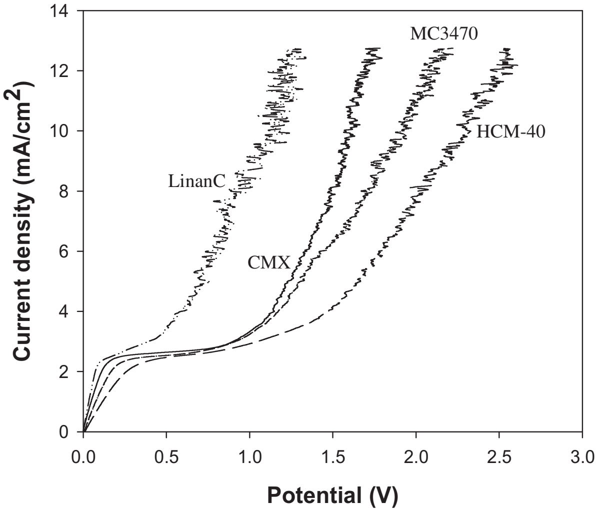
Fig. 4. Relationship between membrane conductivity (κ^m) and solution conductivity (κ_s) for cation-exchange membranes.

Table 4
Isoconductance of cation-exchange membranes

Membrane	Isoconcentration (C_{iso}) (mol/L)	Isoconductance (κ^m_{iso}) (mS/cm)	Volume fraction of inter-gel phase (f_2)
HCM-30	0.50	0.20	0.50
HCM-40	0.45	0.67	0.45
HCM-50	0.43	1.02	0.43
HCM-60	0.40	2.07	0.40
MC3470	0.45	0.78	0.45
LinanC	0.44	0.63	0.44
CMX	0.20	3.88	0.20



(a) Prepared heterogeneous cation exchange membranes



(b) Commercial cation exchange membranes with HCM-40

Fig. 5. Current–voltage curves for prepared heterogeneous cation exchange membranes.

3.2.3. Relationship between heterogeneity and characteristic I–V curve values

The electrical current was supplied by the potentiostat/galvanostat connected to a pair of reference electrodes at a constant current scanning rate, and the potential difference was measured across the membrane. Among electrochemical properties, the limiting current density, resistance ratio, R_3/R_1, and plateau length, ΔV, were evaluated from the current–voltage curve. The shape of the current–voltage curve in an ion exchange membrane presents the experimental conditions, such as concentration, flow rate, and the physicochemical conditions of the membrane surface [24]. The prepared cation-exchange membranes showed a typical pattern consisting of three regions (the ohmic region, the limiting current region, and the over-limiting current region). And a plateau was observed in the current–voltage curve, as shown in Fig. 5. The slope of the current–voltage curve increased again and eventually reached an asymptotic value in the over-limiting current region [24].

Table 5 shows the apparent limiting current density (i_{lim}), R_3/R_1, and ΔV of prepared and commercial cation-exchange membranes. As the amount of ion exchange resin increased in the prepared heterogeneous membranes, the apparent limiting current density and R_3/R_1 increased and the plateau length decreased. Commercial heterogeneous cation-exchange membranes (MC3470 and LinanC) showed a lower value of R_3/R_1 and a shorter plateau length than those of the homogeneous membranes. The results showed that electrochemical properties were closely related to the membrane material and surface characteristics, such as surface charge density and distribution of charged groups.

The apparent limiting current density (i_{lim}) is inversely proportional to the diffusion boundary layer

Table 5
Characteristic values of cation-exchange membranes in current–voltage curves

Membrane	Apparent limiting current density[a] (mA/cm²)	Local limiting current density[b] (mA/cm²)	ΔV (V)	R_3/R_1
HCM-30	1.92	3.31	1.08	2.28
HCM-40	2.35	3.22	0.68	4.52
HCM-50	2.60	3.17	0.67	4.81
HCM-60	2.58	3.11	0.13	5.57
MC3470	2.40	3.16	0.73	3.10
LinanC	2.30	3.03	0.37	5.09
CMX	2.51	2.56	0.73	5.64

[a] Apparent limiting current density was obtained from the corresponding current–voltage curve.

[b] Local limiting current density was estimated by the apparent limiting current density divided by the fraction of the conducting region (ε) in Eq. (4).

Table 6
Electrodialysis performance of cation-exchange membranes in desalting experiments

Membrane[a]	Current efficiency (%)	Average flux (mol/m^2 h)	Power consumption (kWh/mol)
HCM-30	83.4	2.01	0.31
HCM-40	86.3	2.05	0.36
HCM-50	87.7	1.83	0.30
MC3470	85.6	2.15	0.31
LinanC	85.9	1.99	0.30
CMX	95.2	2.05	0.34

[a] The prepared HCM-10, HCM-20, and HCM-60 membranes were not available for the electrodialytic experiments because of a small membrane area.

thickness (δ) and the transport number in the membrane phase (t_m), as shown in Eq. (3):

$$i_{\text{lim}} = \frac{FD}{|t_m - t_{\pm}|}\frac{C_0}{\delta} \tag{3}$$

Here, it is expected that the boundary layer thickness would have the same value under the same hydrodynamic conditions [21]. Therefore, a higher value of the apparent limiting current density represents a small difference between the transport number of the membrane (t_m) and solution ($t_{\pm}$). Thus, the apparent limiting current density of a heterogeneous membrane is predicted to be higher than that of a homogeneous membrane due to a lower value of t_m. However, the heterogeneous membranes showed lower limiting current densities than those of the homogeneous membranes, as shown in Table 5. The difference between predicted and estimated values of the limiting current density is related to the conducting region fraction of the heterogeneous membrane [25]. The local limiting current density in the conducting regions, i^*_{lim}, can be obtained by applying the conducting region fraction in Eq. (4):

$$i^*_{\text{lim}} = \frac{i_{\text{lim}}}{\varepsilon} \tag{4}$$

The value of i^*_{lim} in the homogeneous membrane was higher than those of other heterogeneous membranes, as expected. The local limiting current densities for the prepared heterogeneous cation-exchange membranes also decreased with increasing cation exchange resin content. Thus, the reduced ion-permeable membrane area increased local limiting current density in the conductive region of the prepared heterogeneous cation-exchange membranes.

3.3. *Desalination performance of the heterogeneous cation membranes*

The electrodialytic experiments were carried out in a unit cell pair ED stack consisting of an examined cation-exchange membrane and the common anion-exchange membrane (AMX) in order to investigate the desalination performance of the prepared heterogeneous cation-exchange membranes. The operating current density was set to 2.5 mA/cm^2 based on the local limiting current density in Table 5.

Table 6 summarizes the desalination performance for the cell structures of prepared heterogeneous and commercial cation-exchange membranes in terms of current efficiency, average NaCl flux, and power consumption. The current efficiency of the prepared membranes increased with increasing amount of ion-exchange resin, which is related to ion-exchange capacity and transport number in Table 2. The NaCl flux decreased slightly with increasing amount of resin, which is related to increasing water content. In addition, the power consumption of the prepared membranes decreased due to decreasing electrical resistance as the resin content increased.

The present study showed that the heterogeneity of the prepared ion-exchange membranes was related to the conducting phase in the membranes, which was characterized with various electrochemical properties. And it was shown that membrane properties, such as physicochemical, mechanical, and electrochemical properties, were related to electrodialytic performance. The prepared cation-exchange membranes showed reasonably good performance for the ED process for desalination and water treatment compared to commercially available heterogeneous cation-exchange membranes.

4. Conclusions

In this study, the heterogeneity of prepared membranes, as controlled by the different mixing ratio of the ion-exchange resin to polymeric binder, was estimated based on electrochemical properties such as characteristic values in the current–voltage relationship, electrical conductivity, and chronopotentiometric values. The fraction of the inter-gel phase, f_2, in the membrane structure of the prepared cation-exchange membranes decreased with increasing resin content. The f_2 values of the heterogeneous membranes were 0.4–0.5 and that of the homogeneous membrane was 0.2. The ε values of the heterogeneous membranes, which are related to the conducting region in the heterogeneous structure, increased to 0.6–0.8 as the resin content increased; however, these values were much lower than that of the homogeneous membrane.

In addition, the desalination performance of the prepared cation-exchange membranes was analyzed by the electrodialytic experiments. The results showed that the ratio of the resin to polymeric binder affected current efficiency and NaCl flux, which is related to membrane properties. Through the study, the prepared heterogeneous cation-exchange membranes showed reasonably good performance for desalination and water treatment compared to commercial heterogeneous membranes.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2014.1000386.

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