Charge effectiveness of sulfonated polymer membranes under low-water-content condition

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Abstract

In this study, the effective charge density of a sulfonated polymer membrane was investigated under low-water-content condition in order to develop novel polyelectrolyte membrane for the fuel cell which can be operated without humidification. At first, the sulfonated polymer membranes, which have various water contents and an inhomogeneous fixed-charge distribution, were prepared, and then the membrane potentials across them were measured. The experimental results were analyzed on the basis of the Donnan equilibrium theory and the Nernst–Planck transport equation considering the fixed-charge inhomogeneities in the membrane. It was revealed that the charge effectiveness depended on the water content, the ionic radii of the counterions and the valence of the counterion. In order to interpret the variation of the charge effectiveness depending on those values, the ion-pair theory based on the Fuoss formula was introduced. This approach showed that the ion-pairing effect causes the difference between the effective charge density and the fixed-charge density especially for low-water-content condition.

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1. Introduction

Polyelectrolyte membranes operating under low-water-content condition are important for the development of the fuel cell which can be operating without humidification. There are, however, less fundamental concept and research on this subject at this moment. The low-water-content condition significantly affects the ionic mobility and the interaction between a fixed-charge group and a counterion. In this study, the problems, which occur in the membranes with low-water-contents, are considered.

The fixed-charge density of the charged membrane estimated by the ionic transport procedure is less than that by the equilibrium procedure [1–5]. It has been considered that this phenomenon is a result of the membrane inhomogeneities or ion-pairs between the fixed-charge group and a counterion. In this study, the problems, which occur in the membranes with low-water-contents, are considered.

The fixed-charge density of the charged membrane estimated by the ionic transport procedure is less than that by the equilibrium procedure [1–5]. It has been considered that this phenomenon is a result of the membrane inhomogeneities or ion-pairs between the fixed-charge group and a counterion. Reiss et al. have shown that an inhomogeneous distribution of fixed-charge groups gives rise to increased current efficiency [8,9]. Petropoulos has pointed out that the theory based on structural inhomogeneities of the membranes with a relatively high-water-content appear to be appropriate to explain the difference in the effective charge density obtained by the transport procedure from the net charge density [11]. While the ionic transport phenomena across charged membranes are strongly affected by the fixed-charge groups, the region in the charged membrane, especially for the low-water-content condition or in an organic solvent, is a relatively low dielectric constant. In accordance with the ion-pair theory, most of the fixed-charge groups in the membranes are neutralized by the counterions due to the formation of the ion-pairs [15]. Therefore, the effective charge density is decreased. Chou and Tanioka showed that by considering the ion-pairs between the fixed-charge group and the counterion, the theoretical predictions of the membrane potentials and the permeability coefficients across the membrane in organic solvents are in good agreement with the experimental results [16–18].

In this study, the membrane potentials across the charged membranes, which have various water contents, are
measured in order to understand ionic transport phenomena across the charged membranes under such conditions. According to the studies of Teorell, Meyer and Sievers [19–21], the membrane potentials in a charged membrane can theoretically be expressed by the Donnan equilibrium theory [22,23] and the Nernst–Planck transport equation [24], if it is assumed that the fixed-charge groups are homogeneously distributed in the membrane. In contrast, in the case of inhomogeneous membranes, an additional assumption must be required, for example, a constant ion concentration gradient [25] or a constant electric potential gradient [26] in a membrane. Recently, Mafé et al. developed a theory to analyze the transport properties across membranes with an inhomogeneous fixed-charge distribution [13]. Using this theory, we can calculate the potential difference not only across a homogeneous membrane, but also across an inhomogeneous membrane. Here, we examine the effects of the ion-pairs between the fixed-charge group and the counterion on the charge effectiveness of sulfonated polymer membranes with low-water-contents.

2. Theoretical background

The membrane transport system in this study is shown in Fig. 1. The charged membrane, whose thickness is \( d \), separates two solutions of the same electrolyte. \( C_i(x) \) represents the concentration of the \( i \)th species at a point of coordinate \( x \) within the membrane (\( i = 1 \) for salt cation, \( i = 2 \) for salt anion and \( i = X \) for fixed-charge group). \( C_{li} \) and \( C_{ir} \) denote the concentration of the \( i \)th species in the bulk electrolyte solutions for the left-side cell and the right-side cell, respectively.

The basic equation describing the ionic transport through the charged membrane is the Nernst–Planck equation

\[
J_i = -D_i \left( \frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\phi}{dx} \right)
\]

where \( J_i \) and \( D_i \) are the ionic flux and the diffusion coefficient of the \( i \)th species in the membrane, \( Z_i \) is the valence of the \( i \)th species, and \( \phi \) is the local electric potential in the membrane. In this system, the electric current density should be equal to zero:

\[
z_1 J_1 + z_2 J_2 = 0
\]

The condition of electroneutrality in the membrane and in the bulk electrolyte solutions requires that

\[
z_1 C_1 + z_2 C_2 + z_X C_X = 0
\]
where $C_{ij}$ is the salt concentration in the bulk electrolyte solutions.

According to the Donnan equilibrium, both the ionic concentration and electric potential are assumed to be discontinuous at the membrane–solution interfaces. The electric potentials at the left ($\Delta \phi_L$) and right ($\Delta \phi_R$) interfaces are given as follows:

$$\Delta \phi_L = -\frac{RT}{z_j F} \ln \frac{\gamma_j C_j(0)}{z_j \gamma_k C_k}$$

$$\Delta \phi_R = \frac{RT}{z_j F} \ln \frac{\gamma_j C_j(d)}{z_j \gamma_k C_k}$$

$\gamma_j$ and $\gamma_k$ ($j = L$ and $R$) are the activity coefficients in the membrane and the bulk electrolyte solution, $z_j$ and $z_k$ represent the valence and the partition coefficient of the $i$th species, respectively, $R$ is the gas constant, $T$ is the absolute temperature and $F$ is Faraday’s constant.

At first, it is assumed that the concentration dependence of the activity coefficients of all ions is negligible. The sum of the Donnan potentials ($\Delta \phi_{\text{Don}}$) can then be written as:

$$\Delta \phi_{\text{Don}} = \Delta \phi_L + \Delta \phi_R = -\frac{RT}{z_j F} \ln \frac{C_{j}(0)}{C_{k}(d)}$$

According to the studies of Teorell, Meyer and Sievers, the potential difference across a membrane, which separates the two solutions of different concentrations, can be expressed by the sum of the Donnan potentials at the left and right interfaces and the diffusion potential in the membrane:

$$\Delta \phi = \Delta \phi_L + \Delta \phi_{\text{diff}} + \Delta \phi_R$$

3. Experimental

3.1. Materials

The polyethylene (PE) porous membranes (Hipore H-4050U3) were obtained from Asahi Kasei Corporation, Japan. Styrene and 55% divinylbenzene (mixture of isomers) were purchased from Wako Pure Chemical, Japan. t-Butylperoxy-2-ethylhexanoate (Perbutyl O) was purchased from NOF Corporation, Japan.

3.2. Preparation of the base membranes [27–31]

PE porous membranes were used as the substrate. These membranes were immersed in the monomer solutions, which were composed of styrene, 55% divinylbenzene, and polymerization initiator (Perbutyl O). The mixing ratio of styrene to 55% divinylbenzene was varied to control the membrane water content. The composition of monomer solutions is shown in Table 1. After immersion in the monomer solutions, the membranes were sandwiched between two polyethylene terephthalate films. The copolymerization was then done at 70 °C for 32 h.

3.3. Sulfonation procedure

The base membranes were immersed in concentrated sulfuric acid at 70 °C. To obtain the membranes with different water contents, the sulfonation time was varied. The detailed reaction conditions are listed in Table 1.

3.4. Potentiometric titration and water content measurements

The potentiometric titration measurements were performed using a combination electrode (GST-5721C, TOA, Japan) and a pH meter (HM-60G, TOA, Japan). The apparatus for the potentiometric titration is shown in Fig. 2. First, the membranes were immersed in 2 mol/l HCl solution for 24 h to ensure that the counterions were exchanged for H⁺. After sufficiently washing the membranes in deionized water, two pieces of the membrane (each membrane area was 16 cm²) were soaked in 3 mol/l KCl solution under a nitrogen gas flow with stirring for 1 h to elute the H⁺ ions from the membranes. They were then titrated by adding a 0.1 mol/l KOH solution to obtain the titration curve. The amount of the fixed-charge group, $N_X$ (mol), in the membranes is equal to the titr of KOH.

The membranes used in the potentiometric titration measurements were immersed in 3 mol/l NaCl solution for 24 h to exchange the counterions for Na⁺. The membranes were then sufficiently washed in deionized water. After removing the membrane surface water, the membrane weight in the equilibrium-swollen state, $w_{\text{sw}}$ (g), was measured. Subsequently, the membranes were dried in a vacuum oven at 25 °C for 6 h and the membrane weight in the dry state, $w_{\text{dry}}$ (g), was determined.
The water content of the membranes, \( w_{\text{water}} \) (wt\%), is defined by the following equation

\[
w_{\text{water}} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{wet}}} \times 100
\]  

(9)

The ion exchange capacity, IEC (mol/g dry membrane) and the fixed-charge density, \( C_X \) (mol/l), are determined by the following equations

\[
\text{IEC} = \frac{N_X}{w_{\text{dry}}}
\]  

(10)

\[
C_X = \frac{\rho N_X}{w_{\text{wet}} - w_{\text{dry}}}
\]  

(11)

\( \rho \) is density of water at 25°C (0.99704 \( \times 10^3 \) g/l).

### 3.5. Distribution of the fixed-charge groups across the membrane

An analysis of the fixed-charge distribution across the thickness of the membrane was performed using the energy dispersive X-ray (EDX) attachment (EDAX-PV9900, Philips, Netherlands) of a field emission gun, scanning electron microscope (FE-SEM, S-800, Hitachi, Japan). According to an EDX elemental analysis of sulfur atom along the direction of the membrane thickness, the distribution of the sulfonic acid groups inside the membrane was monitored.

### 3.6. Membrane potential measurements

The apparatus for measurement of the membrane potentials is shown in Fig. 2. A charged membrane was placed in the center of two containers. Both containers were filled with electrolyte solutions of different concentrations; the left container was kept constant at 10\(^{-3}\) mol/l while that on the right varied from 10\(^{-3}\) to 3 mol/l. A voltmeter (HM-40S, TOA, Japan) connected to glass electrodes (HS-205C, TOA, Japan) was used for measurement of the potential difference. Two glass electrodes were placed in saturated KCl solutions, which were connected to the containers by KCl salt bridges. KCl, NaCl, LiCl, CaCl\(_2\) and MgCl\(_2\) were used to measure the membrane potentials.

### 4. Results and discussion

The physicochemical properties of the prepared membranes are summarized in Table 2 with that of a commercial cation-exchange membrane (K501, Asahi Kasei Corporation, Japan) for comparison. The various membranes with different water contents can be obtained by changing the mixing ratio of styrene to divinylbenzene and the sulfonation time. The water content of all prepared membranes is smaller than that of commercial one.

| Membrane | \( w_{\text{water}} \) | IEC    | \( C_X \) | \( d \) |
|-----------|----------------|--------|-----------|-------|
| CEM04     | 3.5            | 0.4    | 11        | 50    |
| CEM07     | 7.2            | 0.3    | 4.6       | 50    |
| CEM16     | 16             | 1.2    | 3.3       | 50    |
| CEM27     | 27             | 1.4    | 1.9       | 50    |
| K501      | 30             | 1.5    | 5.5       | 170   |

\( w_{\text{water}} \) (wt\%), water content of the membrane; IEC (mmol/g dry memb.), ion exchange capacity of the membrane; \( C_X \) (mol/l), fixed-charge density of the membrane; \( d \) (m), membrane thickness.
A cross-sectional SEM image of a cation-exchange membrane (CEM04) with the intensity of the S Kα of the EDX line scan is shown in Fig. 3. According to the EDX elemental analysis of S along the direction of the membrane thickness, most of the fixed-charge groups exist near the membrane surface region. Hence, CEM04 has a fixed-charge density decreasing from the membrane surface to the membrane interior. Similar profiles of the fixed-charge groups are obtained for the others. Hence, we define the dependence of the fixed-charge density on the distance from the membrane surface as follows

$$C_X(x) = C_{X0} \left( \frac{5 - n}{4n} + \frac{5}{4} \left( 1 - \frac{2x}{d} \right)^{\frac{n-1}{n}} \right)^{\frac{n}{4}}.$$  

(12)

where $C_{X0}$ is the maximum value of the fixed-charge density. Note that parameter $n$ represents the degree of the membrane inhomogeneity. Fig. 4 shows that the membrane inhomogeneity increases with $n$ and if the value $n$ equals unity, the membrane is homogeneous. The average fixed-charge density, $C_{Xm}$, is defined as follows:

$$C_{Xm} = \frac{1}{d} \int_0^d C_X(x)dx = \frac{C_{X0}}{n}.$$  

(13)

The average fixed-charge density can be experimentally obtained by the potentiometric titration measurements and thus the maximum value of the fixed-charge density can be calculated by solving Eq. (13).

Fig. 5 shows the typical experimental results for the membrane potentials for CEM07. The membrane potentials are also calculated using Eqs. (1)–(3), (7) and (8) and are plotted in Fig. 5 as a solid line for the membrane model with an inhomogeneous fixed-charge distribution ($n > 1$) and as a dotted line for the homogeneous membrane model ($n = 1$). The calculation results using the homogeneous

![Fig. 3. Cross-sectional SEM image of a cation-exchange membrane (CEM04) with the distribution of sulfonic acid group from EDX analysis.](image)

![Fig. 4. Theoretical model for the distribution of the fixed-charge groups across the membrane for different values of $n$.](image)

![Fig. 5. Membrane potentials of CEM07 for the various electrolytes as a function of the salt concentration in the bulk electrolyte solutions ($C_{sL}$). O, Δ, ■, ●, and ▲ represent the experimental data for KCl, NaCl, LiCl, CaCl₂, and MgCl₂, respectively. Solid lines indicate the theoretical results obtained by fitting the experimental data to Eqs. (1)–(3), (7) and (8) considering the inhomogeneous fixed-charge distribution in the membrane. Dotted lines are the theoretical results obtained by fitting the experimental data to Eqs. (1)–(3), (7) and (8) neglecting the inhomogeneous fixed-charge distribution in the membrane.](image)
membrane model do not agree with the experimental data. In contrast, taking the inhomogeneous fixed-charge distribution into account in the membrane potential theory, the theoretical estimations are in good agreement with the experimental results. The values of the charge effectiveness, $Q$, estimated by fitting the experimental results to the theoretical ones are shown in Table 3. Most of the $Q$ values do not equal unity. This means that we must consider not only the membrane inhomogeneity, but also another reason such as the electrostatic interaction between the fixed-charge group and counterion to explain the difference in the effective charge density from the fixed-charge density.

In accordance with the ion-pair theory, ionic transport phenomena across charged membranes are strongly affected by the fixed-charge groups, since the region in the charged membrane is a relatively low dielectric constant. Thereby most of the fixed-charge groups in the membranes are neutralized by the counterions due to the formation of ion-pairs. As a result, the effective charge density is decreased. The $Q$ value is related to the association constant ($K_A$) between the fixed-charge group ($X$) and the counterion ($A$) in the membrane and expressed by Eq. (15) as a function of $K_A$:

$$
X + A \rightarrow XA \quad \text{(14)}
$$

$$
Q \sim \frac{1}{K_A + 1} \quad \text{(15)}
$$

Application of the Fuoss formalism [32,33] to the ion-pair in a membrane would lead to the association constant

$$
K_A = \frac{4\pi N_A}{3 \times 10^{-3}} a_{AB}^3 \exp \left( \frac{z_A z_B q^2}{4\pi e e_A a_{AB} k_B T} \right) \quad \text{(16)}
$$

where $N_A$ is Avogadro’s number, $q$ is the electronic charge, $e_A$ and $e_B$ are the dielectric constant of the vacuum and solvent, respectively, $a_{AB}$ is the center-to-center distance between ions, and $k_B$ is the Boltzmann constant. From Eq. (15), the more the fixed-charge groups in the membrane pair with the counterions, the more the effective charge density is decreased. Fig. 6 shows the $K_A$ dependence on $a_{AB}$ in the 1–1 type electrolyte system. From Fig. 6, $K_A$ is increased as the center-to-center distance $a_{AB}$ increases. For the ion-pair in a membrane, the fixed-charge groups pair with the counterions. Therefore, the order of the center-to-center distance is determined by the ionic radii of the counterions. $K_A$ calculated for the 1–1, 2–2, and 3–3 type electrolyte systems are given in Table 4. It shows that $K_A$ for ions with a higher valence is greater than that for ions with a lower valence. Besides, $K_A$ is related to the dielectric constant near the fixed-charge groups and plotted as a function of the dielectric constant in Fig. 7. $K_A$ increases with the decreasing dielectric constant. In accordance with Booth [34], the dielectric constant is dependent on the electric field. Hence, in the membrane, the dielectric constant near the pore surface is lower than that of the bulk value due to the electric field generated by the fixed-charge and decreased as the surface charge density of the membrane pore surface increases. The surface charge density is related to the fixed-charge density; if the membrane has a cylindrical pore with a uniformly distributed fixed-charge, the surface charge density of the membrane pore surface is given as follows [35,36]

$$
\sigma = \frac{F r_0 C_X}{2} \quad \text{(17)}
$$

where $\sigma$ is the surface charge density and $r_0$ is the pore radius. Therefore, the surface charge density is in proportion to the fixed-charge density of the membrane or is inversely proportional to the membrane water content. As a result,
the 1–1 type electrolyte system calculated by Eq. (15) for $\epsilon = 1$, $z_B = -1$, $T = 298.15 \, \text{K}$ and $\sigma_{AB} = 2.5 \, \text{Å}$. $K_A$ increases with the increment of the fixed-charge density of the membrane or the membrane water content decrease.

Desnoyers and his coworkers [37] proposed a structural hydration interaction (SHI) model based on that effect to account for the many thermodynamic properties of small solutes in water. Satoh et al. [38] applied the SHI model to the study of the counterion binding of polyelectrolytes in order to explain the experimental fact that the specific counterion binding was not observed in the polysulfate and polysulfonate/Mg$^{2+}$, Ca$^{2+}$ systems but in the polysulfate and polysulfonate/K$^+$ systems, though the electrostatic interaction between the fixed-charge group and divalent ion was stronger than that between the fixed-charge group and monovalent ion. For this reason, the $Q$ value for CEM07, CEM16, and CEM27 measured in KCl solution is the smallest of all electrolytes. For CEM04, the dielectric constant near the fixed-charge groups seem to be so small that the electrostatic interaction between the fixed-charge group and the counterion overcomes the effect of hydration on the solute–solvent interaction between them because of the low-water-content. The agreement cited above suggests that ion-pairs between the fixed-charge group and counterion in the membrane cause that the effective charge density estimated by the ionic transport procedure is less than the fixed-charge density especially for low-water-content condition.

5. Conclusions

A study on charge effectiveness of a sulfonated polymer membrane with a low-water-content was carried out in order to obtain the fundamental knowledge for the development of the fuel cell which can be operating without humidification. At first, the membrane potentials across the charged membrane, which has various water contents and an inhomogeneous fixed-charge distribution, were measured. The experimental results were analyzed on the basis of the Donnan equilibrium theory and the Nernst–Planck transport equation considering the fixed-charge inhomogeneities in the membrane. The results show that the value of the charge effectiveness will depend on the membrane water content, the ionic radii of the counterions and the valence of the counterion. Secondly, to interpret the variation in the value of the charge effectiveness, we attempted to introduce the concept of the ion-pair between the fixed-charge group and counterion inside the membrane. Compared with the experimental results, the prediction of the ion-pair theory qualitatively agreed with the experimental tendency. This suggests that ion-pairs cause the difference between the effective charge density and the fixed-charge density especially for low-water-content conditions. Further discussion is required to quantitatively estimate the effect of the ion-pair on the ion transport behavior through the charged membranes.

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