Distribution of $H^+$ and $OH^-$ Ion Concentration and of Specific Electric Conductance in a Water Dissociation Layer Formed in an Ion Exchange Membrane

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(Manuscript submitted March 20, 2007; accepted May 16, 2007)

Abstract

Distribution of $H^+$ and $OH^-$ ion concentration and of specific electric resistance in a water dissociation layer formed in an ion exchange membrane was evaluated using the theoretical equation and electrodialysis experimental results. The change of the concentration in an anion exchange membrane was larger than that in a cation exchange membrane. When $Mg(OH)_2$ was precipitated on the cation exchange membrane, the change was increased. The intensity of the water dissociation reaction is accelerated due to the auto-catalytic reaction caused by quaternary ammonium groups in the anion exchange membrane or metallic hydroxides precipitated on the cation exchange membrane.

Key words: ion exchange membrane, electrodialysis, water dissociation,

1. Introduction

In ion exchange membrane electrodialysis, electrolyte concentration at the desalting surface of an ion exchange membrane decreases owing to the concentration polarization and the concentration at the solution/membrane surface reaches zero at limiting current density. At over limiting current density water dissociation occurs. The water dissociation is noticed in an electrodialysis process because it decreases current efficiency and gives rise to scale troubles, and it attracts an attention in a bipolar membrane or an electrodeionization process because it increases current efficiency. The water dissociation reaction is first observed by Kressman et al.[1] and Frilette [2]. Rosenberg et al.[3] observed current density vs. pH relationship and found that the reaction in the cation exchange membrane is weaker than that in the anion exchange membrane. The mobility of cations is generally less than that of anions in an electrolyte solution, so that the concentration polarization is generally recognized to occur more easily in the cation exchange membrane than in the anion exchange membrane. Because of this reason, it is expected that the water dissociation occurs more easily in the cation exchange membrane than in the anion exchange membrane. However, contrary to this expectation, it has been recognized that the water dissociation occurs more easily in the anion exchange membrane, and it is recognized that the violent water dissociation occurs when metallic hydroxides are precipitated on the cation exchange membrane.
In the previous investigation [4], we discussed the mechanism of water dissociation reaction with the experimental work assuming that the water dissociation reaction generates in the water dissociation layer formed on the desalting surface of the ion exchange membrane. In this investigation the intensity of the water dissociation was divided into the intensity of the second Wien effect [5] and the auto-catalytic reaction, and it was found that the intensity of the second Wien effect is negligible. The mechanism of the auto-catalytic reaction is unknown at present, but it was recognized that the intensity of the auto-catalytic reaction caused by quaternary ammonium groups in the anion exchange membrane is larger than that caused by sulfonic acid groups in the cation exchange membrane. Further it was confirmed that the intensity of the water dissociation reaction is increased drastically due to the auto-catalytic reaction of the metallic hydroxides such as Mg(OH)\textsubscript{2} or Fe(OH)\textsubscript{3} precipitated on the desalting surface of the cation exchange membrane[4].

In this investigation, we evaluate the distribution of H\textsuperscript{+} and OH\textsuperscript{-} ion concentration and the specific electric conductivity in the water dissociation layer and discuss the effects of the functional groups in the membrane and metallic hydroxides on the water dissociation reaction succeeding to the previous investigation.

2. Theoretical

2.1 H\textsuperscript{+} ion and OH\textsuperscript{-} ion concentration in the water dissociation layer

Under an unapplied electric potential field, the water dissociation is an equilibrium reaction as follows [6].

$$H_2O \leftrightarrow H^+ + OH^- \quad k_a = 2 \times 10^{-5} \text{s}^{-1} \quad k_b = 1.5 \times 10^{14} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$$

(1)

$k_a$ and $k_b$ are respectively the forward and reverse reaction rate constant. With an applied electric potential field, $k_a$ is assumed to increase due to the Wien effect [7] and the catalytic reaction [8,9], whereas $k_b$ remains being constant. At over limiting current, the water dissociation layer is formed near the membrane surface as shown in Fig. 1.

Fig. 1 Formation and transport of H\textsuperscript{+} and OH\textsuperscript{-} ions in a water dissociation layer.
We assume here that H⁺ and OH⁻ ions are generated and transported in the water dissociation layer. The generation rate of H⁺ ions $\sigma_H$ (mol/cm²s) at $x = 0 - x$ (cm) is

$$\sigma_H = \int \left( k_a C_{H2O}^0 - k_b C_H C_{OH}^0 \right) dx = k_a C_{H2O}^0 x - k_b \int C_H C_{OH}^0 dx$$  \hspace{1cm} (2)

The generation rate of OH⁻ ions $\sigma_{OH}$ at $x = x - l$ is

$$\sigma_{OH} = \int \left( k_a C_{H2O}^0 - k_b C_H C_{OH}^0 \right) dx = k_a C_{H2O}^0 (l - x) - k_b \int C_H C_{OH}^0 dx$$  \hspace{1cm} (3)

$C_H$, $C_{OH}$ and $C_{H2O}^0$ (mol/cm³) are the concentration of H⁺ ions, OH⁻ ions and H₂O at x. $l$ (cm) is the thickness of the water dissociation layer.

The flux of H⁺ ions $J_H$ and OH⁻ ions $J_{OH}$ (mol/cm²s) are given by the Nernst-Planck equation as follows.

$$J_H = -D_H \frac{dC_H}{dx} - \frac{FD_H C_H}{RT} \frac{d\phi}{dx}$$  \hspace{1cm} (4)

$$J_{OH} = -D_{OH} \frac{dC_{OH}}{dx} + \frac{FD_{OH} C_{OH}}{RT} \frac{d\phi}{dx}$$  \hspace{1cm} (5)

where $D_H$ and $D_{OH}$ (cm²/s) are the diffusion constant of H⁺ and OH⁻ ions, $F$ is the Faraday constant, $R$ is the gas constant and $\phi$ (V) is the electric potential at x.

From the mass balance in Fig. 1, the following formulae hold between the generation and transport of H⁺ and OH⁻ ions.

$$\sigma_H = J_H = \left( \frac{i}{F} \right) \eta_H$$  \hspace{1cm} (6)

$$\sigma_{OH} = -J_{OH} = \left( \frac{i}{F} \right) \eta_{OH}$$  \hspace{1cm} (7)

where $i$ (A/cm²) is current density, $\eta_H$ and $\eta_{OH}$ are current efficiency for H⁺ and OH⁻ ions respectively.

$C_H$ and $C_{OH}$ are introduced from Eqs. (2) – (7) as:

$$C_H = \sqrt{\frac{u_{OH} C_{OH}^0 C_H^0}{u_H}} \exp \left\{ \frac{F}{2RT} i \nu l(2\xi - 1) \right\}$$  \hspace{1cm} (8)

$$C_{OH} = \sqrt{\frac{u_H C_H^0 C_{OH}^0}{u_{OH}}} \exp \left\{ -\frac{F}{2RT} i \nu l(2\xi - 1) \right\}$$  \hspace{1cm} (9)
in which, \( u_H \) and \( u_{OH} \) (cm\(^2\)/Vs) are mobility of H\(^+\) and OH\(^-\) ions, \( \nu \) (\( \Omega \) cm) is the specific electric resistance of the water dissociation layer, \( \xi \) is \( x/l \) and \( T \) is the absolute temperature.

### 2.2 Specific electric conductivity in the water dissociation layer

Specific electric conductivity in the water dissociation layer \( \lambda \) (S/cm) is given by the following equation assuming H\(^+\), OH\(^-\), Na\(^+\) and Cl\(^-\) ions are dissolved in a solution.

\[
\lambda = \lambda \eta + \lambda (1 - \eta) \quad (10)
\]

Here, \( \eta = \eta_H \) for the cation exchange membrane and \( \eta = \eta_{OH} \) for the anion exchange membrane. \( \lambda \eta \) and \( \lambda (1 - \eta) \) are respectively contribution of dissociated ions; H\(^+\), OH\(^-\), and dissolving electrolyte ions; Na\(^+\), Cl\(^-\), to \( \lambda \), and they are respectively presented by the following equations.

\[
\lambda \eta = F(u_H C_H + u_{OH} C_{OH}) \quad (11)
\]
\[
\lambda (1 - \eta) = F(u_{Na} C_{Na} + u_{Cl} C_{Cl}) \quad (12)
\]

Substituting Eqs. (8) and (9) into Eq. (11) gives:

\[
\lambda = \frac{2F}{\eta} \sqrt{u_H u_{OH} C_H^0 C_{OH}^0} \cosh \left( \frac{F}{2RT} \nu l (2\xi - 1) \right) \quad (13)
\]

Specific electric conductivity of the water dissociation layer \( \Lambda \) (S/cm) is introduced by integrating \( \lambda \) within the range of \( \xi = 0 - 1 \) as follows.

\[
\Lambda = \int \lambda d\xi = \frac{4RT}{\eta \nu l} \sqrt{u_H u_{OH} C_H^0 C_{OH}^0} \sinh \left( \frac{F}{2RT} \nu l \right) \quad (14)
\]

### 3. Experimental

#### 3.1 Experiment 1

A sample cation exchange membrane (Selemion CMR, sulfonic acid type, Asahi Glass Co.) or an anion exchange membranes (Selemion ASR, quaternary ammonium type) was incorporated with the experimental electrodialysis unit. Electric current density \( i \) was applied through Ag-AgCl electrodes supplying a NaCl solution. Current efficiency of water dissociation reaction \( \eta \) was measured from the pH change in the concentrating cell. Effective electric resistance \( \nu l \) (\( \Omega \) cm\(^2\)) of the water dissociation layer was calculated for the cation exchange membrane using the following equation:

\[
\nu l = \frac{pH + (1/2) \log(u_{OH}/u_H) C_H^0 C_{OH}^0}{(F/2RT)i \log e} = \frac{7.123 - pH}{8.4515i} \quad i < 0 \quad (15)
\]
v l for the anion exchange membrane is calculated by

\[ v l = \frac{pH - 14 - (1/2) \log(u_H / u_{OH}) C_H^0 C_{OH}^0}{(F/2RT)i \log e} = \frac{pH - 7.123}{8.4515i} \quad i > 0 \] (16)

\( \lambda \) were calculated by substituting \( v l \) into Eq.(13).

Fig. 2 gives \( C_H \) or \( C_{OH} \) versus \( \xi \) (= x/l). The change of \( C_H \) and \( C_{OH} \) in the water dissociation layer in the anion exchange membrane is larger than that in the cation exchange membrane. The accelerated water dissociation in this experiment is estimated to be caused by the auto-catalytic reaction of the quaternary ammonium groups or sulfonic acid groups. The intensity of the auto-catalytic water dissociation reaction caused by the quaternary ammonium groups is stronger than that caused by the sulfonic acid groups. Fig. 3 shows \( \lambda \) versus \( \xi \) obtained in this experiment. \( \lambda \) is increased at both ends in the water dissociation layer and decreased at the middle in the layer. This phenomenon occurs because \( H^+ \) and \( OH^- \) ion concentration increases at both ends in the layer.

Water dissociation layer thickness \( l \) described in the title of Fig. 3 is determined by calculating \( \lambda \) using Eq. (14) and substituting \( v \) (= 1/\( \lambda \)) into Eqs. (15) or (16). \( l \) is invariable with the change of current density and its values are considerably large. Because of this increased \( l \) value, potential gradient in the water dissociation is decreased and the intensity of the Wien effect becomes negligible [4].

3.2 Experiment 2

\( \text{Mg(OH)}_2 \) was precipitated on a sample cation exchange membrane (Aciplex K-102, sulfonic acid type, Asahi Chemical Co.), supplying a 0.05M \( \text{MgCl}_2 \) solution into a desalting side of the membrane and passing an electric current above limiting current density. \( C_H \), \( C_{OH} \) and \( \lambda \) were measured in the same way as described in Experiment 1 and compared to the data of the \( \text{Mg(OH)}_2 \) non precipitated (control) membrane.

Fig. 4 gives \( C_H \) or \( C_{OH} \) versus \( \xi \). Larger change of \( C_H \) and \( C_{OH} \) for the \( \text{Mg(OH)}_2 \) precipitated cation exchange membrane is due to the auto-catalytic reaction of \( \text{Mg(OH)}_2 \) precipitated on the cation exchange membrane. The change of \( \lambda \) in this experiment is shown in Fig. 5, indicating drastic decrease of \( \lambda \) at the middle of the water dissociation layer formed in a \( \text{Mg(OH)}_2 \) phase. Similar experimental data are observed when \( \text{Fe(OH)}_3 \) is precipitated on the surface of the cation exchange membrane.

References

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Fig. 2  $H^+$ and $OH^-$ ion concentration distribution in a water dissociation later formed on a cation and an anion exchange membrane.

- $\bigcirc$: $C_{H^+}$, $\bigtriangleup$: $C_{OH^-}$
- Open: Selemion CMR  Filled: Selemion ASR
- 0.01 M NaCl 0.131 A/cm²

Fig. 3  Specific electric conductivity distribution in a water dissociation layer formed on a cation and an anion exchange membrane.

- $\bigcirc$: 0.104, $\bigtriangleup$: 0.131, $\bullet$: 0.261 A/cm²
- Open: Selemion CMR $l = 8.4 \times 10^{-5}$ m
- Filled: Selemion ASR $l = 4.8 \times 10^{-5}$ m
- 0.01 M NaCl

Fig. 4  $H^+$ and $OH^-$ ion concentration distribution in a water dissociation later in Mg(OH)$_2$ precipitated on a cation exchange membrane.

- $\bigcirc$: $C_{H^+}$, $\bigtriangleup$: $C_{OH^-}$
- Open: control  Filled: Mg(OH)$_2$ precipitated
- 0.02M NaCl 0.10 A/cm²

Fig. 5  Specific electric conductivity distribution in a water dissociation layer in Mg(OH)$_2$ precipitated on a cation exchange membrane.

- $\bigcirc$: 0.1, $\bigtriangleup$: 1.0 A/cm²
- Open: control $l = 5.3 \times 10^{-5}$ m
- Filled: Mg(OH)$_2$: precipitated $l = 5.6 \times 10^{-5}$ m
- Aciplex K-102, 0.02 M NaCl