

pH 미세전극을 이용한 이온교환막 표면에서의 pH 측정

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pH measurement in the vicinity of an ion-exchange membrane with a pH-microelectrode

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1. Introduction

Concentration polarization (CP) of an ion-exchange membrane has been examined in numerous theoretical and experimental studies [1,2]. This phenomenon is caused by the difference in ion transport numbers between the electrolyte solution and the ion-exchange membrane. As a limiting current density (LCD) is reached during a membrane operation, depletion of counter ions is more pronounced. At the LCD, the complete depletion and an abrupt increase in potential across the membrane induce water dissociation phenomena. The water dissociation can lead to changes of pH and aquatic chemistry of the solution, resulting in some problems such as scaling of inorganic ions on the membrane surface and membrane damage. Although several hypotheses of the water dissociation phenomena have been proposed such as the Second Wien effect and a field-enhanced chemical reaction of protonation and deprotonation, no direct measurement of pH in the vicinity of the membrane has been reported. An ion-selective microelectrode is a powerful tool for the direct measurement of local concentration of the target ion in micro-environment [3].

The purpose of this study is to investigate water dissociation phenomena occurring at the interface of the membrane and electrolyte solution by measuring pH profiles within DBL as a function of distance from the membrane using the pH-microelectrode in the region of under and over the LCD.

2. Background

An ideal ion-selective microelectrode shows a linear relationship between the electrode voltage and the ion activity on the log scale. This relationship is described mathematically by the Nernst equation:

$$E_{io} = E' + \frac{RT}{zF} \ln \left[\frac{[A]_o}{[A]_i} \right], \quad (1)$$

where E_{io} is the potential difference between the inside (i) and outside (o) solutions, E' is a constant reference potential, z is the valence of ion A (square brackets designate the activity of A), and R , T , and F the gas constant, the absolute temperature, and the Faraday constant, respectively. In the ion-selective microelectrode, $[A]_i$ represents the ion activity of the backfilling solution which is kept constant. Hence, Eq. (1) can be rewritten and simplified to the following form for a monovalent cation at 25 °C:

$$E_{io} = E' + 59 \log[A^+]_o. \quad (2)$$

Eq.(2) predicts that, for the ideal ion-selective microelectrode calibrated by standard solutions, the resulting potential of the electrode increases linearly with A ion concentration on the log scale, with the slope of 59 mV/pH at 25 °C.

3. Experimental

The pH sensitive polymeric microelectrodes with 25 μm of a tip diameter were prepared according to conventional method [4]. PVC (Mw=102,000) was mixed with the hydrogen ion-exchanger (i.e. hydrogen-ion ionophore liquid membrane (Fluka, 95293)) and the quantity of PVC was about 10% of the final mixture. The calibration was carried out with a series of buffer solutions with

pH ranging from 2 to 11. The potential was measured by an electrometer (Dual Differential Electrometer FD 223, World Precision Instruments, WPI) and recorded by a data recording system (Duo 18, WPI).

A current-voltage curve of the CMX cation-exchange membrane (CEM) was obtained using a two-compartment cell. The pH in the vicinity of the membrane facing the desalting compartment was measured with the pH-microelectrode moved by a micromanipulator. Dilute KCl solution (0.025 M) was used as the electrolyte in each measurement.

4. Results and Discussion

Fig. 1 shows the calibration curve in the pH range of 2 to 11. In the pH range of 4 to 10, the slope of the curve is 56 mV/pH which is close to 59 mV/pH (ideal value). It is common that polymeric membrane microelectrodes have the upper and lower detection limits for the measurement of ionic concentration [5]. In this study, the upper detection limit at which diversity from the linearity (a dashed line in Fig. 1) begins is approximately pH 3 and the lower one pH 11.

The LCD of the CMX membrane in the experimental cell was 26.5 A/m². Fig. 2 and Fig. 3 show the potential difference arising from the pH change due to the water dissociation under and over the LCD, respectively. It is noted that the potential difference is observed even under the LCD as shown in Fig. 2, implying that the water dissociation occurs. It is inconsistent with the water dissociation theory [6]. However, this water dissociation under the LCD is negligible (the proton flux calculated by the Nernst-Planck equation is approximately 10⁶ mol/m²-sec).

As shown in Fig. 3, the potential differences increases exponentially with approaching to the membrane at current densities over the LCD. As a result, it can be directly observed that the water dissociation occurs at the interface of the membrane and electrolyte solution in the desalting compartment as hypothesized [6]. The results indicate that the water dissociation begins to occur near the LCD and becomes more pronounced over the LCD. Furthermore, the characteristic region in which the proton concentration significantly changes is widen with increasing the current density, ranging from 20-70 μm from the membrane.

5. Acknowledgement

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6. References

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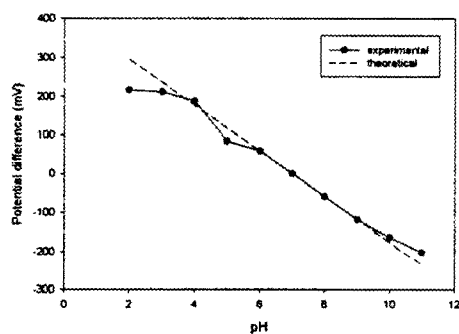


Fig. 1. The calibration curve of pH-microelectrode

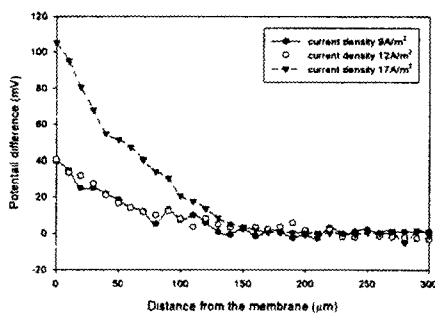


Fig. 2. The potential profiles with the distance from the membrane at various current densities under the LCD

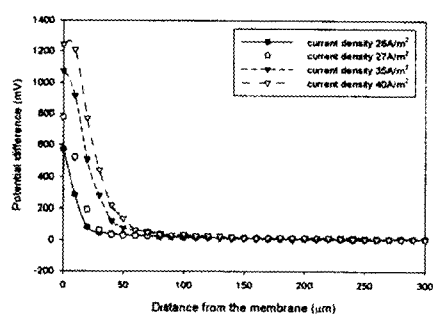


Fig. 3. The potential profiles with the distance from the membrane at various current densities near and over the LCD