

전도성 고분자 전해질막을 이용하는 전기화학적 시스템의 임피던스 해석

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Impedance analysis of electrochemical systems using an ion-conducting polymer electrolyte membrane

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1. Introduction

Ion-conducting polymer electrolyte membranes (PEMs) have recently used in developing fuel cell or solar cell for portable, mobile and residential applications [1]. Polymer electrolyte membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), alkaline electrolyte fuel cell (AFC) and dye-sensitized solar cell have been employing the ion-conducting PEMs to complete their electrical circuits to produce electricity.

Fuel or solar cell has many heterogeneous interfaces to complete its electrical circuit. The interfaces are mainly comprised of PEM/catalyst and catalyst/electrode. At their interfaces, there are several sub-interfaces involving ionic diffusion, charge transfer, and/or electrochemical reaction. They cause voltage drop to give rise to cell irreversibilities. In order to precisely evaluate the performance of the fuel or solar cells, it is needed to investigate the electrochemical relationship at the interfaces.

Many researchers have proven that an electrical impedance

spectroscopy (EIS) is a non-invasive technique to characterize: (i) the electrical properties of materials, electrochemical phenomena and structural observations of bipolar membranes [2], (ii) composite membranes [3] and (iii) synthetic ion-exchange membranes [4]. Taking into account the space resolution below 1 nm, the impedance measurements enable to investigate very thin sub-layers such as the interfaces in an ion-conducting PEM system.

In this study, we suggest how to apply for impedance analysis in the electrochemical system using the ion-conducting polymer electrolyte membrane. Impedance spectra of the basic electrochemical system consisting of an ion-conducting PEM and aqueous electrolyte were investigated in light of its main dielectric and phenomenological structures. Based on the impedance results, an equivalent circuit was suggested to describe the structures of the ion-conducting PEM system (ICPEMS).

2. Experimental

Potassium chloride (Sigma, St. Louis, Missouri) in reagents grade was used as a supporting electrolyte. The KCl solutions with different concentrations were used for measurement of the electrical impedance spectra of an ion-exchange membrane used in this study. Deionized water (18 M Ω -cm) was used in preparing all the electrolytes.

The Neosepta AMX (Tokuyama Soda Co., Japan) is a reinforced standard grade homogeneous polymer electrolyte membrane. Their main properties are presented in the brochure of the manufacturer [5]. Prior to all the experiments, the test membranes were immersed in the desired electrolyte solution for 24 hrs to reach its equilibrium status.

The electrical impedance spectroscopy was obtained using the electro-dialytic cell which consisted of two compartments of equal volume (150 mL) separated by the PEM that was supported by rubber gaskets across a circular hole of 0.785 cm². The details are found elsewhere [6].

Sinusoidal alternating currents (ACs) were supplied to a pair of Ag/AgCl planar electrodes with 0.1 mA amplitude in the frequency range from 10⁶ to 10⁻³ Hz for measurements of impedance spectra by a

potentiostat/galvanostat (AutoLab, Model PGSTAT 30, Netherlands). The Ag/AgCl planar electrodes minimize the water dissociation reactions at the electrodes, which may affect the composition of electrolytes in the compartment for both experiments, as well as the high impedance by the electric double layer of electrodes at very low frequencies for the measurement of the impedance spectra. The potential difference and impedance across the membrane system were measured using two Ag/AgCl electrodes immersed into Luggin capillaries. All the experiments were conducted at 25 ± 1 °C.

3. Results and Discussion

3.1. Impedance arising from the ion-conducting PEM system

The sinusoidal AC responded to the several superimposed electric fields in the ICPEMS: local fields around the PEM, diffusion boundary layers, double layers on the phase boundaries and externally formed fields. Fig. 1 shows the typical Nyquist plot of the ICPEMS examined in this study. At lower frequencies (below 139 Hz), the diameter of the second capacitive loop (the smaller semicircle above the abscissa) decreased in the presence of stirring, corresponding to the impedance by ion diffusion in the diffusion boundary layer (DBL). This implies that the first capacitive (the larger semicircle above the abscissa) and the following inductive loop (the semicircle below the abscissa) were due to the geometric effect of the electrochemical cell used in this study. Fig. 1 shows that the stirring results in decreasing impedance by diffusion because it significantly decreases the thickness of a DBL. In addition, no second capacitive loop was observed for the impedance spectrum obtained from the same electrolytic cell without the ion-exchange membrane, and just the first capacitive and the following inductive loops appeared (not shown here). Including the stirring effects, it can be inferred that, at low frequencies (below 139 Hz), the second capacitive loop depicts the electrical responses to the ion-exchange membrane and the electrolyte solution as well as the interface phenomena (e.g., DBL).

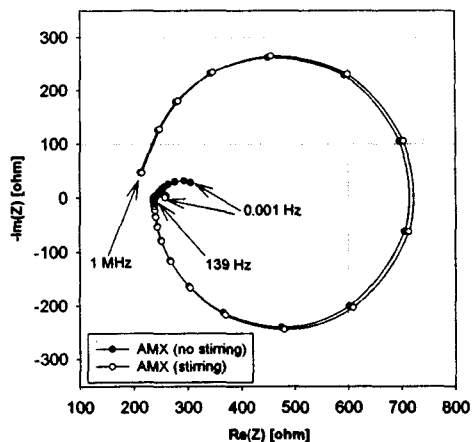


Figure 1. Stirring effect on the impedance spectra (Nyquist plots) of the AMX membrane in 0.01 M KCl using the two-compartment electrolytic cell [6] when solutions in each compartment were stirred and not (0.1 mA, amplitude 10^6 to 10^{-3} Hz, frequency range).

3.2. Equivalent circuit of the ion-conducting PEM system

Capacitive or inductive loops are often generalized as depressed semicircles by parallel R (resistance)- Q (constant phase element, CPE) circuits, expressing different relaxation times in a complex electrochemical system. The CPE impedance is obtained using the following equation in the impedance representation:

$$Q(\omega) = -\text{Im}(Z) = Y_o(j\omega)^{-n} \quad (1)$$

where, Y_o is the admittance ($\Omega\text{-sec}^{-n}$) and n the empirical parameter ($0 < n < 1$). When $n=0.5$, 1 and -1 , the CPE is called a Warburg impedance, which is associated with a diffusion process according to Fick's law, a reactance by capacitance and one by inductance, respectively [4, 7].

The power dependency of the constant phase element can be observed in the plot of $1/\omega$ vs. $-\text{Im}(Z)$ in which the slope is the reciprocal of total admittance. The two distinct parallel R - Q circuits were analyzed in the frequency range examined in this study. The

linear relationship on ω^{-1} in the frequency range from 139 to 16.8 Hz indicated the pure capacitance characteristic according to the Eq. (1). On the other hand, at very low frequencies from 11 to 0.001 Hz, the fractional power of the reactance was to be approximately 0.5, implying the Warburg impedance, which was proportional to $\omega^{-0.5}$. Thus, the capacitor and diffusion characteristics might result from effects of the heterogeneous ionic transport and the DBL effect, respectively. Hence, it can be suggested that the three components are electrochemically connected in series in the ion-conducting PEM system as illustrated in Fig. 2.

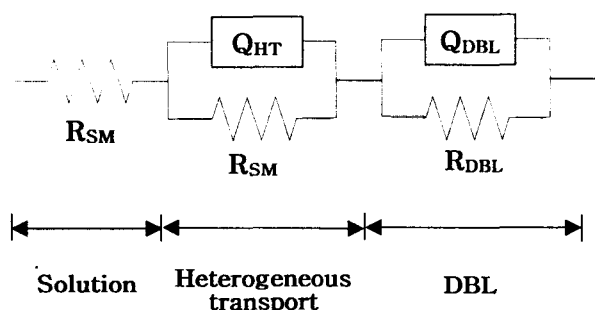


Figure 2. Equivalent circuit for the ion-conducting PEM system used in this study, which consists of effects of the membrane immersed in solution (SM), heterogeneous transport (HT) and diffusion boundary layer (DBL).

Fig. 3 shows good agreement between the experimental data of the AMX membrane system in the 0.01 M KCl solution and the fitting results using the suggested equivalent circuit (see Fig. 2).

4. Conclusion

The impedance spectroscopic study enabled to confirm the microscopic phenomena qualitatively and quantitatively and provided useful information on the interfacial phenomena of the ICPEMS. Thus, it is suggested that the electrical impedance spectroscopy gives rise to a promising way to investigate phase boundaries and ionic transport phenomena in the fuel cells using PEMs.

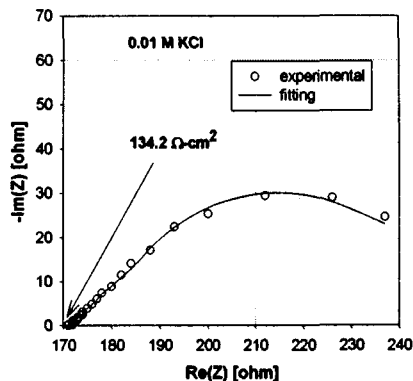


Figure 3. Impedance spectra of the AMX membrane in 0.01 M KCl using the two-compartment electrolytic cell under no stirring. The impedance data of a high frequency region (above 139 Hz) were omitted. (0.1 mA, amplitude 10^6 to 10^{-3} Hz, frequency range).

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