Influence of CO_2 dissolution into anion exchange membrane on fuel cell performance

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ABSTRACT

Influence of CO_2 dissolution into anion exchange membranes (AEMs) on fuel cell performance was investigated. The conductivity of AEM decreased with an increase in carbonate ion species. For the power generation test with a supply of humidified H_2/O_2, the IR–free cell potential difference for the membrane electrode assembly (MEA) with the HCO_3^- form membrane was lower than that with the OH-form membrane. This low cell potential difference became noticeable by the supply of CO_2 to either anode or cathode. The increment of ohmic resistance was confirmed by the supply of CO_2 to cathode, but no obvious change in ohmic resistance was observed by the supply of CO_2 to anode. Then, a CO_2 permeation flux was determined by a gas chromatograph analysis of exhaust gas, and the correlation between the AEM fuel cell performance and the composition of ion species in the membrane was discussed.

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1. Introduction

Recently, anion exchange membranes (AEMs), which are alkaline polymers containing anion exchange sites (e.g. ammonium, phosphonium, or sulfonium base) have been developed as the electrolytes of fuel cells [1,2]. In the AEMs, ion species such as OH^- and CO_3^{2-} serve as charge carriers. As compared with the proton exchange membrane fuel cells (PEMFCs), anion exchange membrane fuel cells (AEMFCs) have advantages in the ease of oxygen reduction reaction on cathode and the possible use of non-precious metal electrocatalysts [3–5]. The performance enhancement of AEMFCs was achieved by developing the anion exchange ionomer to enlarge the three-phase boundary for the electrochemical reaction [6,7]. The maximal power density of AEMFCs attained was reported to be ca. $823\,mW\,cm^{-2}$ at $60\,^\circ C$ with a feed of humidified H_2 and O_2 to the anode and cathode, respectively [8].

For the fuel cells with alkaline electrolytes, however, the absorption of CO_2 into the electrolyte is a major concern to the unstable power generation. For the alkaline fuel cells using an aqueous KOH electrolyte, CO_2 dissolution into the electrolyte gives rise to serious performance degradation due to the precipitation of carbonate salts in the vicinity of electrodes [9,10]. In this respect, AEMFCs are preferable since the absence of free cations like K^+ in the electrolyte membrane excludes the possibility of carbonate precipitation [11,12]. In fact, Kohl et al. have successfully demonstrated

the stable power generation of AEMFC with a feed of 67% CO_2 – 33% O_2 gas mixture to the cathode [13,14]. However, CO_2 dissolution into the AEM resulted in degradation of the cell performance to some extent. In the previous reports, the effect of CO_2 in the cathode feed gas on power generation characteristics of AEMFCs was evaluated, and the increases in the ohmic resistance and electrode overpotential were observed with a rise in CO_2 concentration [15,16]. Although this degradation can be explained by the formation of carbonate ion species (CO_3^{2-} and HCO_3^-) in the membrane, detailed experimental evidences have not been reported.

In this study, the influence of carbonate ion species on the cell performance was evaluated precisely, and the degradation factors of AEMFC performance under the feed of CO_2-containing gases were discussed.

2. Experimental

2.1. Ion-exchange of AEM

The basic properties of AEM (A201, Tokuyama Co.) used in this study were described in the previous report [17]. The thickness and the ion exchange capacity (IEC) of the membrane was $28\,\mu m$ and $1.7\,mmol\,g^{-1}$, respectively. The as-received AEM with HCO_3^- form was ion-exchanged to obtain the membranes containing various compositions of carbonate ion species. In this report, "carbonate ion species" collectively means CO_3^{2-} and HCO_3^-. The term of "carbonate ion" or "bicarbonate ion" corresponds to CO_3^{2-} or HCO_3^-, respectively. For the ion-exchange of AEM, the aqueous solutions of KOH,

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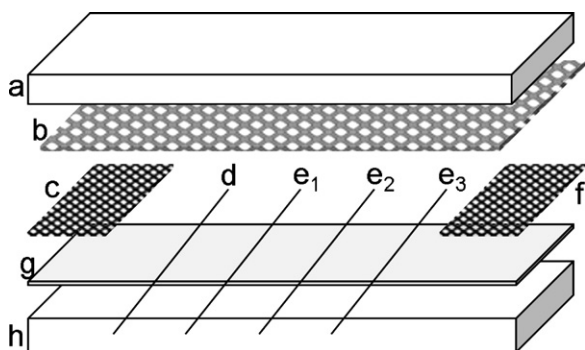
Fig. 1. Schematic diagram of the cell for electrolyte conductivity measurement: (a and h) silicone plate; (b) PTFE mesh; (c and f) platinized platinum mesh; (d and e) platinum wire; (g) AEM.

K_2CO_3, and $KHCO_3$ in various ratios ($K^+ = 1.0$ M) were prepared. The equivalent fraction of carbonate ion species to K^+ in this aqueous electrolyte (x_{CO_3}) is given by Eq. (1).

$$x_{CO_3} = \frac{\left[CO_{3aq}^{2-}\right] + \left[HCO_{3aq}^{-}\right]}{\left[K_{aq}^{+}\right]} \tag{1}$$

where $[X_{aq}]$ is the molar concentration of ion species, X, in the aqueous electrolyte. The anion exchange membranes were immersed in 50 ml of these solutions for more than 6 h at room temperature. The amount of the anion species in the immersed solution was ca. 1000 times of the IEC of AEM used for fuel cell test (size: 66 mm × 75 mm, IEC: 50 μmol). The equivalent fraction of carbonate ion species to quaternary-ammonium base ($-N(CH_3)_3^+$) in AEM (y_{CO_3}) is given by equation (2).

$$y_{CO_3} = \frac{\left[CO_{3m}^{2-}\right] + \left[HCO_{3m}^{-}\right]}{\left[-N(CH_3)_{3m}^{+}\right]} \tag{2}$$

where $[X_m]$ is the molar concentration of ion species, X, in the electrolyte membrane.

The initial equivalent fraction, $y_{CO_3}^0$, was determined by the acid-base titration under an Ar atmosphere to prevent the CO_2 dissolution into AEM and aqueous solution. The ion-exchanged AEM was rinsed several times with distilled water and immersed in 1.0 M NaCl aqueous solution for more than 6 h in order to ion-exchange to Cl^- form. After this chemical treatment, OH^- and carbonate ion species were completely eluted from AEM. Then, the content of carbonate ion species in the membrane was determined by Warder titration of the resultant aqueous solution. The indicators used for the first and second equivalence points were the phenolphthalein solution and bromocresol green-methyl red mixed solution, respectively, and 0.01 M HCl was used for the titrant. The molar amount of carbonate ion species was given by the titration volumes of 0.01 M HCl at the first equivalence point (V_1) and at the second equivalence point (V_2); $0.01 \times (V_2 - V_1)$. As the molar concentration of $-N(CH_3)_3^+$ is described by the following Eq. (3), the molar amount of $-N(CH_3)_3^+$ was $0.01 \times V_2$. Then, $y_{CO_3}^0$ can be calculated by Eq. (4).

$$\left[-N(CH_3)_{3m}^{+}\right] = \left[OH_m^{-}\right] + 2\left[CO_{3m}^{2-}\right] + \left[HCO_{3m}^{-}\right] \tag{3}$$

$$y_{CO_3}^0 = \frac{V_2 - V_1}{V_2} \tag{4}$$

2.2. Electrolyte conductivity measurement

The conductivity of ion-exchanged AEM (size: 10 mm × 70 mm) was measured at 50 °C with the four – probe cell shown in Fig. 1. The cell consisted of two separated platinized platinum mesh with

a gap of 50 mm and four platinum wires (0.5 mm in diameter) with intervals of 10 mm. The cell was placed in a glass tube where the humidity was controlled at 95% relative humidity (RH) by mixing of the dry and water-saturated N_2 gases. The electrolyte resistance was measured by impedance spectroscopy (Solartron 1260 frequency response analyzer) and derived from the real part at a frequency of 10 kHz. In the preliminary experiments, the impedance plot at this frequency was confirmed to be sufficiently close to the real axis for exclusion of electrode polarization. The impedance spectra were collected with three different membrane lengths of 10, 20, and 30 mm using the four platinum wires. The resistance of membrane per unit length (R/l) was determined by the slope of these data plots for measured resistance vs. membrane length. The conductivity of AEM was calculated by Eq. (5).

$$\sigma_{AEM} = \frac{l}{RS} \tag{5}$$

where σ_{AEM} is the ionic conductivity of AEM, and S is the cross-sectional area of the membrane.

2.3. Fuel cell test

Pt/C (Pt 46.4 wt.%, Tanaka Kikinzoku Kogyo) was used for the electrocatalyst as received. Membrane electrode assembly (MEA) was prepared by screen-printing the mixture of Pt/C and anion exchange ionomer (AS-4, 5% in propanol, Tokuyama Corp.) on AEM. The detailed procedure for preparation of MEA was described in the previous report [17]. The electrode area was 5 cm^2, and the both amounts of ionomer and Pt loading were 0.5 mg cm^{-2} in the electrodes. Ion-exchange treatment of MEA was carried out in the same manner as described in Section 2.1. The ion-exchanged MEA was rinsed several times with distilled water and set in a fuel cell housing in an Ar atmosphere. AEMFC configuration for power generation test was also shown in the previous report [17]. The fuel cell experiments were carried out at 50 °C. The gaseous mixture of 80% H_2–x% CO_2–(20 − x)% N_2 ($x = 0, 2, 5, 10$) was fed to the anode, and 21% O_2–x% CO_2–(79 − x)% N_2 ($x = 0, 2, 5, 10$) was fed to the cathode at a flow rate of 100 ml min^{-1}. H_2 (purity: 99.99%) was fed from the hydrogen generator (HG 260B, GL Sciences,). O_2 (purity: 99.995%), N_2 (purity: 99.999%), and CO_2 (purity: 99.99%) were used as received. The feed gases were humidified by bubbling through water at 50 °C. Electrochemical measurements were conducted with Solartron 1287 potentiostat and Solartron 1260 frequency response analyzer. The ohmic resistance and the cell potential difference were recorded at constant current densities at 0–0.2 A cm^{-2} for 10 min unless otherwise noted. The measurement was carried out in the ascending order of the current density. The real part at the frequency of 10 kHz in the impedance spectra was used as the ohmic resistance. The composition of exhaust gas from the fuel cell was analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector (VARIAN, TCD, CP-490). Steam in the exhaust gas was trapped by a condenser at 0 °C before gas analysis. A Propak Q column was used for the separation of CO_2, and a molecular sieve 5A column for the separation of H_2, O_2, and N_2.

3. Results and discussion

3.1. Conductivity of AEMs containing various ratios of carbonate ion species

To observe CO_2 absorption and the carbonate ion formation in the membrane, OH^-–form AEM ($y_{CO_3}^0 = 0.1$) was exposed to the ambient air (ca. 400 ppm CO_2). Fig. 2 shows the time course of the equivalent fraction of carbonate ion species to quaternary-ammonium base in AEM (y_{CO_3}). The carbonate ion, CO_3^{2-}, was