



Water transport characteristics of the passive direct formic acid fuel cell



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HIGHLIGHTS

- The water transport characteristics of the DFAFC were investigated.
- The water flux of DFAFC increased with the increasing current density.
- The water flux of DFAFC decreased with the decreasing membrane thickness.
- The water transport characteristics of the DFAFC differed from those of DMFC.

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ABSTRACT

The water transport characteristics of the passive DFAFC were investigated to obtain a general understanding of the water transport characteristics through the membrane in the DFAFC in this study. Effects of the current density, membrane thickness and formic acid concentration on the water flux through the membrane in the passive DFAFC were investigated and they were compared with those of the DMFC and the PEFC. It was found that the water crossover through the membrane of the passive DFAFC linearly increased with increasing current density irrespective of the membrane thickness similar to the DMFC; however, the water flux was smaller than that of the DMFC. Referring to the effect of the membrane thickness on the water flux, the water flux from the anode to the cathode increased with increasing the membrane thickness in the DFAFC, although it decreased with increasing membrane thickness in the DMFC. Moreover, the water flux increased with decreasing fuel concentration in the DFAFC, although the water crossover in the DMFC was not influenced by the fuel concentration. From these results, it was found that the water transport characteristics in the DFAFC were different from those in the DMFC.

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1. Introduction

Direct formic acid fuel cells, DFAFCs, have received considerable attention as an alternative power source for electric portable devices due to their high power density which is comparable to that of the PEMFC, polymer electrolyte fuel cell operated with hydrogen–oxygen, and 6 times that of direct methanol fuel cells, DMFCs [1–3]. Moreover, it is broadly known that the fuel crossover rate in the DFAFC is lower than that in the DMFC [4–7]. On the other hand, the water transport characteristics which are a key factor in stable and efficient operation of a fuel cell using a polymer electrolyte membrane in the DFAFC have not been revealed.

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It has been recognized that water management is a critical issue for the performance and durability of a fuel cell employing the polymer electrolyte membrane because sufficient water content is necessary to maintain the high proton conductivity of the membrane. On the other hand, excessive liquid water can block the pores of the catalyst and gas diffusion layer and may cause flooding. Typically, the water management in a PEMFC stands for a balance of water in between membrane hydration and cathode flooding [8,9]. However, the problem is more challenging for a DMFC. Water management in a DMFC refers to providing water for the anode, while preventing cathode flooding. Unlike the hydrogen fuel cells, membrane hydration is not an important issue in DMFCs as long as water is provided from the methanol solution [10]. Especially, when the DMFC is operated in a passive mode which does not use a pump and/or blower for supplying a fuel and oxygen, the water management becomes more serious because the liquid water, which is produced by the cathode reaction and methanol oxidation reaction due to the methanol crossover at the cathode, is likely to

accumulate in the cathode. Therefore, numerous studies of the water transport characteristics in the PEMFC [11–13] and DMFC [14–16] have been carried out. On the other hand, to the best of our knowledge, there have been no reports about the water transport characteristics in the DFAFC. Because the DFAFC does not use water for the anode reaction and the high concentration of formic acid shows a hygroscopic property [17], the water transport characteristics are likely to differ from those in the DMFC. Of course, the water transport characteristics in the DFAFC are also likely to differ from those of the PEMFC because the DFAFC uses a liquid fuel for the anode. Therefore, it is necessary to investigate the water transport characteristics in the DFAFC and compare them to those of the DMFC and PEFC.

This work aims to achieve a general understanding of the water transport characteristics through the membrane in the DFAFC. The passive DFAFC with the insertion of a hydrophobic filter (HF) at the cathode surface was used in this study for two reasons. First, the passive DFAFC was suffered from serious flooding [18] so that the investigation of the water transport characteristics of the passive DFAFC is more important than those of the active DFAFC. Second, we demonstrated that the flooding could be improved and the current density was increased by inserting the hydrophobic filter at the cathode surface in our previous study [18]. From this result, the HF enables measuring the water crossover (WCO) of the passive DFAFC over a wide range of current density. Using this structure, the effects of the membrane thickness, formic acid concentration and current density on the WCO were investigated by measuring the WCO during a 2 h operation. Two different operations were conducted to measure the water crossover in the wide range of current density: the 2 h power generations at a different constant voltage with and without HF and the 2 h operations at the same constant voltage using a different HF containing different amounts of fluorinated ethylene propylene copolymer (FEP). Finally, the water transport characteristics were compared with those of the DMFC and the PEMFC to characterize the water transport characteristics of the passive DFAFC.

2. Experimental

2.1. Membrane electrode assembly (MEA) preparation

NR 212, Nafion 115 and Nafion 117 (Dupont) were used as the polymer electrolyte membrane. In order to activate the proton conductivity, the membranes were pretreated by sequential immersion in boiling solutions of 3 vol-% H_2O_2 for 1 h, de-ionized water for 1 h, 0.5 mol l^{-1} H_2SO_4 for 1 h, and de-ionized water for 1 h, in that order. Palladium black (Alfa Aesar) and platinum black (HiSPEC 1000, Johnson Matthey Fuel Cells Co., Ltd.) were used as the catalysts for the anode and the cathode, respectively. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and 5 wt% Nafion solution (Wako Pure Chemical Industries, Ltd.). For the anode, the Pd ink was coated on the microporous layer, which was prepared with 1 mg cm^{-2} of a carbon black containing 10 wt% Nafion on the carbon cloth (35% Teflonized, ElectroChem, Inc.) to form the electrode. For the cathode, the Pt ink was coated on the carbon paper (35% Teflonized, ElectroChem, Inc.) with a microporous layer in a similar manner. The catalyst loadings were 6 mg cm^{-2} for Pd, the anode, and Pt, the cathode, respectively. The ionomer loadings of the catalyst layer were 15 wt% for the anode and 10 wt% for the cathode. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min. The projected area of the electrode was 4.84 cm^2 (2.20 × 2.20 cm).

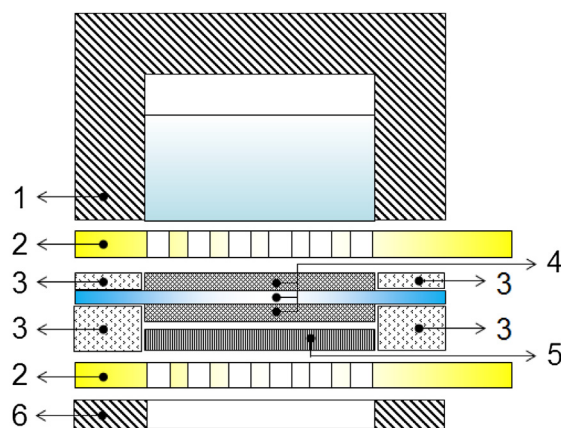
2.2. Cell structure and hydrophobic filter

Fig. 1 shows a schematic diagram of the passive DFAFC cell used in this study. A fuel reservoir, 12 cm^3 in capacity, was prepared in the anode compartment. The MEA was sandwiched between the two current collectors, which were plates of stainless steel, 1 mm, coated with gold, having open holes, and a 74% open ratio.

In some operations, the hydrophobic filter, HF, 5, was inserted between the cathode and the cathode current collector. The HFs which have different hydrophobicity were prepared by coating a carbon black layer, 1 mg cm^{-2} carbon black on the carbon paper (35% Teflonized, ElectroChem, Inc.) with FEP, fluorinated ethylene propylene copolymer, and heating them to 100 °C for 1 h. The FEP coating was repeated several times until the FEP content reached a certain weight. Table 1 shows the loading of the FEP and the contact angle of the HF. The contact angle was measured by a contact angle meter (CA-X, Kyowa Interface Science Co., Ltd.), and the hydrophobicity increased with the increasing FEP loadings. The projected area of the filter was 4.84 cm^2 which was the same as that of the electrodes.

2.3. Measurement of the power generation characteristics

The DFAFC was operated in a complete passive mode, i.e., the cathode was air breathing and the fuel was supplied from the tank to the anode electrode without a pump. All experiments were conducted under the room conditions, 1 atm, 293–298 K. A formic acid solution was prepared by diluting formic acid (special grade reagent, Wako Pure Chemical Industries, Ltd.) with distilled water (Kyoei Pharmaceutical Co., Ltd.). The current versus time, $i-t$, characteristics were also measured at different cell voltages, 0.3 V, 0.4 V and 0.5 V. All the electrochemical measurements were conducted using an electrochemical measurement system (Hz-5000, Hokuto Denko, Co., Ltd.). The entire cell weight and the concentration of the solution were also measured at the beginning and the end of the $i-t$ measurements to calculate the formic acid and water crossovers using the precision balance (GF-600, A&D Company, Limited). When the cell weight was measured after the $i-t$ operation, water droplets were removed from the cathode surface to obtain an accurate weight loss of the fuel since the accumulated water droplet likely causes an overestimation of the final cell weight. The formic acid concentration was measured by gas chromatography equipped with a TCD detector and a Porapak T column (Shimadzu, GC14-B).



1: Anode tank, 2: Current collector, 3: Rubber Sheet
4: MEA, 5: Hydrophobic Filter, 6: Cathode cover

Fig. 1. Schematic diagram of the passive DFAFC cell.

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