

Control of methanol transport and separation in a DMFC with a porous support

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Abstract

The effect of porous support properties such as porosity ε and water absorptivity α_w on the methanol crossover (MCO) and transport phenomena through the membrane electrode assembly (MEA) of a direct methanol fuel cell (DMFC) under open circuit conditions was theoretically and experimentally investigated. Porous plates, made of different materials, with different properties, were used as the support of the DMFC, and the performance of the crossover, i.e., CO₂ production rate at the cathode, cell temperature, fluxes of water and methanol, through the MEA with or without the porous plate were measured and compared to each other. The methanol flux increased with the increasing product of ε and α_w , $\varepsilon\alpha_w$, and the water flux slightly decreased with its increase, in the range where $\varepsilon\alpha_w$ was over a certain value, suggesting that the methanol flux was controlled by the diffusion resistance through the porous plate, whereas the total flux was not affected by it. It was clearly shown that these porous plates prevented the passive DMFC from undergoing a significant loss of methanol due to the crossover, and also being out of temperature control. © 2006 Elsevier B.V. All rights reserved.

Keywords: Passive DMFC; Methanol crossover; Porosity; Water absorptivity; Cell temperature; Porous plate

1. Introduction

There has been an increasing demand for the development of direct methanol fuel cells (DMFCs) [1–3] because of their high energy densities which are suitable for mobile electric devices and automobiles. However, the energy density of the DMFCs currently under development is still far from that expected due to the methanol crossover and the high overvoltage at the electrodes [4,5]. Due to the methanol crossover, the DMFC usually shows the highest performance at low concentrations of methanol from 2 to 3 M [6,7] under the active conditions. To overcome the methanol crossover, a large number of studies [8–12] were carried out for developing a new proton-conducting membrane with a low methanol permeability and high proton conductivity. Modification of the existing membranes like Nafion has also been conducted by making it a composite membrane [13–15] with inorganic or organic materials, surface modification by physical treatment [16] or by coating the surface with a thin film [17–19]. Only a few papers considered the reducing ability in methanol

crossover by mass transport control in the backing layer [20,21].

Recently, passive DMFCs, that suck methanol from a reservoir by an osmotic action and breath air from its surrounding by natural convection and diffusion, have been demonstrated, and the performance was investigated by some researchers under different conditions [20,22–32]. The reports on the passive DMFCs revealed some different performance behaviors compared to that of active DMFCs. For example, a methanol concentration like 5 M, which is higher than that for an active DMFC, was sometimes assigned as the optimum condition for the i - V performance [18,27,33]. An air-breathing DMFC with a thinner membrane exhibited a better i - V performance at low current density [34]. The power density calculated on the basis of the unit area of the electrode for a stack was much better than that of the single cell [23]. A passive vertically oriented DMFC always produced a better performance than that horizontally oriented [35]. These behaviors were attributed to the methanol crossover that induced an increase in the cell temperature due to the exothermic reaction between the permeated methanol and the oxygen at the cathode, so that the polarization was reduced, and hence, a high performance was achieved [23,34,35]. These do not suggest that the methanol crossover played a desirable role in the passive DMFC.

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It should be noted that the methanol crossover causes a loss of the methanol and significantly reduced the energy density and the efficiency of the DMFC. In the passive DMFCs, the methanol crossover and the temperature of the cell were not controlled, which sometimes leads to fatal damage to the cell.

The authors demonstrated, in a recent report [20], that a passive DMFC with a porous carbon plate as a support reduced the methanol crossover and constantly controlled the cell temperature. In the experiment, two different types of porous carbon plates were used, and their methanol crossover reductions were different suggesting that the properties of the porous plate affected the methanol crossover. The mechanism of reducing the MCO was explained by the diffusion control of the methanol through the porous plate. This study is primarily focused on a theoretical consideration for the reduction of the methanol crossover through the MEA with a porous plate. The behavior of the transport and separation of methanol through this type of passive DMFC under open circuit conditions was then investigated. Experiments were conducted to show the unique properties of this cell by measurement of the MCO using different porous materials, i.e., porous carbon and porous alumina, with different properties, e.g., pore structures, water absorptivity, at different methanol concentrations and different temperatures.

2. Theoretical consideration of the mass transfer through MEA

2.1. Mass flow rate of the solution

When an MEA with a polymer electrolyte membrane like Nafion is in contact with a methanol solution and air at both surfaces, the crossover of methanol and also water occurs. The mass flow rate of the solution M_T , a mixture of methanol and water, through the MEA would be controlled by the rate of removal of the solution from the cathode surface into the cathode gas due to vaporization under open circuit conditions, in some cases. The driving force of the vaporization is the difference in vapor pressure of the solution between the cathode surface and the flowing gas and the rate of vaporization, v_1 , can be expressed as follows:

$$v_1 = k(p_v - p_a) \quad (1)$$

$$= k(p_0 \exp(-L_a/(RT)) - p_a) \quad (2)$$

where k is a constant, p_v the vapor pressure of the solution at the meniscus of the porous cathode, p_a the vapor pressure of the cathode gas, p_0 the vapor pressure of the bulk solution, and L_a is the latent heat of vaporization of the solution. Eq. (2) was derived from the Clausius–Clapeyron relation.

The solution that exists at the cathode was a mixture of methanol and water, and the total flux across the membrane J_T consists of a methanol flux J_M and a water flux J_W :

$$J_T = J_M + J_W \quad (3)$$

and also, as the total flux is controlled by the rate of vaporization, and hence:

$$J_T = M_T/A = v_1/A \quad (4)$$

where A is the area of the membrane. The methanol flux can be related to the water flux based on the general relationship in flux between a solute and a solvent that permeate through a membrane as follows:

$$J_M = (1 - \sigma)C_m^*J_W - D_{mM}(dC_m/dx) = J_{CM} + J_{DM} \quad (5)$$

The first term of Eq. (5) is the convection flux of methanol J_{CM} with the water flux and the second term shows the diffusion flux of methanol J_{DM} , where σ is the reflection coefficient, and C_m^* is the average concentration of methanol in the membrane and D_{mM} is the diffusion coefficient of methanol in the membrane, and C_m is the methanol concentration at position x in the membrane from the surface.

Methanol that usually permeated to the cathode is oxidized by oxygen into water with the help of a catalyst, and the methanol concentration at the cathode surface remained low. Under this situation, the diffusion flux, J_{DM} is increased by the increase of difference in the methanol concentration between both surfaces of the membrane. This raised the methanol flux J_M , while the total flux was constant, i.e., reducing the flux of water, because the total flux was controlled by the rate of water vaporization as shown by Eqs. (3) and (4). As a result, methanol preferentially permeated through the membrane, and this caused a significant loss in energy density and energy efficiency of the DMFC.

2.2. Methanol diffusion through a porous plate

Let us now consider a case where a porous plate, which absorbs water into the body by osmotic action, is used as a support of the MEA on the anode side. When the flow rate of the solution through the MEA driven by the evaporation of water at the cathode is not very high, the porous plate is not a resistance for the transport of the total solution through the porous plate and MEA, if the porous plate absorbs sufficient water. In addition, the flux of methanol through the membrane can be controlled by the diffusion resistance of the porous plate. This mechanism can reduce the diffusion flux of methanol through the membrane J_{DM} by reducing the methanol concentration at the anode surface resulting in reducing the difference in the methanol concentration between the surfaces of the membrane. The diffusion flux of methanol controlled by the porous plate can be given by Fick's law as follows:

$$J_{DM} = -D_{\text{eff},M}(\Delta C_M/\Delta X) \quad (6)$$

where $D_{\text{eff},M}$ is the effective diffusion coefficient of methanol through the porous plate, and ΔC_M is the difference in the concentrations of methanol between both sides of the porous plate with thickness ΔX .

The effective diffusion coefficient $D_{\text{eff},M}$ depends on the properties of the porous plate where the coefficient is proportional to the porosity of cross-section ε_s and inversely proportional to the tortosity τ of the porous plate as follows:

$$D_{\text{eff},M} = kD_M\varepsilon_s/\tau \quad (7)$$

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