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Numerical investigation of spatial variation of hydrophobicity in diffusion media along the through-plane direction in direct methanol fuel cells

Geonhui Gwak [a], Kise Lee [a], Junhee Lee [a], Suwon Lee [b], Hyunchul Ju [a,*]

[a] Department of Mechanical Engineering, Inha University, 100 Inha-ro, Nam-Gu, Incheon 402-751, Republic of Korea
[b] Department of Energy Engineering, Inha University, 100 Inha-ro, Nam-Gu, Incheon 402-751, Republic of Korea

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ABSTRACT

The wetting characteristics of the diffusion media (DM) of direct methanol fuel cells (DMFCs) are studied using a one-dimensional (1-D) DMFC model. The model, which is based on the capillary transport theory for porous media, facilitates investigation of the impact of spatial variation of hydrophobicity in the DM on methanol transport/crossover and the resultant cell performance. The 1-D DMFC simulation results were compared with the empirical data acquired at a methanol feed concentration of 8 M. The theoretical simulations agree well with the experimental data and also indicate that methanol crossover from the anode to the cathode can be decreased by employing an anode DM design in which the hydrophobicity increases toward the anode catalyst layer. Under the anode DM design, a maximum power density of 73.15 mW cm^{-2} was predicted by the model at a methanol feed concentration of 8 M, i.e. sufficiently close to the experimental measurement (71.17 mW cm^{-2}). Detailed simulation results clearly show that the reduced methanol crossover is mainly derived from liquid transport characteristics; the rate of liquid transport through the DM is reduced as the liquid flows from the relatively hydrophilic region to the relatively hydrophobic one. This numerical study demonstrates that the present DMFC model is a valuable tool for the design and optimization of DM with spatial wettability variation to effectively control the methanol and water transport in DMFCs.

Introduction

Methanol crossover in direct methanol fuel cells (DMFCs) has been extensively studied over the past decade with the aim to improve the DMFC performance and fuel efficiency. The development of novel anode catalysts and membranes has been actively pursued in order to overcome the slow kinetics of the methanol oxidation reaction (MOR) and/or resolve the issue of high methanol permeation from the anode to cathode regions [1–9]. Recently, Nam et al. [8] showed that the use of silica-supported Pt–Ru catalysts in the anode side helped to

* *Corresponding author*. Tel.: +82 32 860 7312; fax: +82 32 868 1716.
E-mail address: hcju@inha.ac.kr (H. Ju).
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reduce the methanol crossover at high methanol feed concentrations of 5-10 M. Paneri et al. [9] fabricated the hybrid membranes wherein the graphene oxide membrane was sandwiched by two Nafion 211® membranes. They reported that the membranes led to considerable DMFC performance improvements at the methanol feed concentrations of 5 M and 10 M.

Novel designs of anode diffusion media (DM) have been proposed for an effective control of methanol and water transport inside DMFCs with the ultimate aim to achieve low methanol crossover [10–23]. Liu et al. [10] emphasized the importance of the wettability of the anode microporous layer (MPL) for obtaining favorable water profiles inside DMFCs. They found that increasing the hydrophobicity of the anode MPL was effective for enhancing the backflow of water from the cathode to the anode, thereby reducing the methanol concentration in the anode electrode via dilution, with the consequent improvement of the cell performance. Shaffer et al. [11] developed a one-dimensional (1-D), two-phase DMFC model and theoretically analyzed the effects of the hydrophobic anode MPL on water crossover through the membrane. The simulation results suggested that the hydrophobic anode MPL contributes to achieving a lower liquid saturation level in the anode catalyst layer (CL), which subsequently reduces the water transport via an electro-osmotic drag (EOD) and enhances the back diffusion of water from the cathode. Zago et al. [12] utilized theoretical and experimental approaches to explore the impact of the anode MPL on water and methanol transport in DMFCs. Specifically, they compared the relative contributions of diffusion, hydraulic permeation, and EOD to the overall methanol and water crossover through the membrane. Yang et al. [13] fabricated membrane electrode assemblies (MEAs) with/without the anode MPL and then compared their performance using in situ polarization and electrochemical impedance spectroscopy (EIS) measurements with variations in the operating current densities, methanol feed concentrations, and air flow rates. They found lower kinetic losses in both the anode and cathode regions when the anode MPL is used because of the reduction in methanol crossover owing to the anode MPL. An empirical analysis of the effects of a hydrophobic anode MPL via polarization tests by Kang et al. [14] demonstrated that the cell performance was significantly improved by the hydrophobic anode MPL under high methanol feed concentration conditions, whereas the cell performance was lower when the anode MPL was used under low methanol feed concentration conditions. Therefore, they concluded that methanol transport toward the anode CL was effectively limited by the anode MPL.

Although the aforementioned hydrophobic MPLs were composed of carbon black (CB) mixed with a PTFE binder, other researchers attempted to include additional carbon materials within the MPL to further improve the efficacy of the MPL for enhancing the DMFC performance [15–18]. Wu et al. [15] and Yuan et al. [16] utilized carbon nanotubes (CNTs) as a filler for the anode MPL. Wu et al. [15] fabricated a crack-free MPL using multiwalled CNTs and thus achieved reduced water crossover from the anode to the cathode. Based on an empirical assessment, Yuan et al. [16] demonstrated that the addition of CNTs into the anode MPL was beneficial in terms of charge transport, anode catalyst utilization, and methanol transport during DMFC operations. Kim et al. [17] indicated the requirement for a crack-free anode MPL in order to reduce methanol crossover in DMFCs operating under high methanol-feed concentration conditions. They showed that the number of cracks in the MPL could be significantly reduced by adding platelet carbon nanofibers (PCNFs) to the MPL slurry, and a maximum power density of 67.7 mW cm^{-2} was achieved at 7 M methanol feed concentration with the anode MPL made of 50 vol% CB and 50 vol% PCNF. Yuan et al. [18] suggested the three-layer structure of anode DM i.e. combined with the woven carbon-fiber fabric (WCFF), carbon paper, and carbon-powder MPL and highlighted that the WCFF layer facilitated the removal of CO_2 bubbles in the anode side of DMFCS.

Although favorable water and methanol distributions and the resultant higher DMFC performance were achieved by using the MPLs, the multilayered electrode designs based on the MPL technology are vulnerable to delamination of the MEA layers during long-term DMFC operation, which substantially increases the contact resistance between the layers, resulting in high ohmic loss and local hot spots in the MEA. Therefore, a one-layer electrode design would be beneficial for achieving higher cell performance and extended durability. Our previous studies [24,25] demonstrated that liquid transport in porous DM was effectively controlled by spatial variation of the hydrophobicity of the DM in the cell thickness direction.

Based on the liquid transport characteristics, Kang et al. [26] designed and fabricated a new anode DM wherein the spatial variation of PTFE loading along the DM thickness was achieved by using the spray coating-based new water-proofing DM treatment. Superior DMFC performance was achieved with the new anode DM design at high methanol feed concentrations.

In this study, the effectiveness of the special anode DM design is quantitatively assessed based on the formulation of a new transport term related to the spatial variation of the hydrophobicity; this term is incorporated into the 1-D, two-phase DMFC model developed in a previous study [27]. The main emphasis is placed on accurately predicting the water and methanol transport processes through the special anode DM and the resultant methanol crossover and overall cell performance. Herein, the advanced 1-D DMFC model is first validated against the experimental data acquired by Kang et al. [26], and then detailed species distributions, with or without the special DM treatment, are further analyzed in order to obtain a better understanding of the role of variation of DM hydrophobicity. This numerical study demonstrates that the present DMFC model is a valuable tool for the design and optimization of the spatial hydrophobicity variation of the DM for an effective control of methanol and water transport in DMFCs.

Numerical model

Model assumptions

The specific assumptions used in the model are as follows:

(1) The gas phase obeys the ideal gas law, which is valid because all the gases in the DMFC are maintained at a low pressure relative to their respective critical pressures.