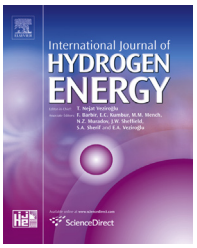
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–12

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Analyzing the effects of fluctuating methanol feed concentration in active-type direct methanol fuel cell (DMFC) systems

Geonhui Gwak [a], Kise Lee [a], Saad Ferekh [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

ARTICLE INFO

Article history:
Received 12 July 2014
Received in revised form
2 December 2014
Accepted 12 January 2015
Available online xxx

Keywords:
Methanol feed concentration
Direct methanol fuel cell
Methanol crossover
Active DMFC systems
One-dimensional DMFC model

ABSTRACT

In active-type direct methanol fuel cell (DMFC) systems, the methanol feed concentration inevitably fluctuates for various reasons, such as inaccuracy in the methanol sensors or the complexity of injecting additional methanol and/or water into the anode fuel recirculation loop. In this study, we use theoretical computations to examine the effects of fluctuating methanol feed concentration on the time-dependent behavior and resultant cell performance of DMFCs. Using a one-dimensional (1-D) two-phase transient thermal DMFC model, we conducted 1-D transient simulations under various DMFC operating conditions with different anode/cathode stoichiometries, cell operating temperatures, and cathode inlet humidification conditions. The simulation results clearly address the influences of these operating parameters on the evolution of cell voltage, cell temperature, methanol crossover, and overall efficiency, highlighting that fluctuation in methanol concentration on the DMFC performance induces fluctuations in these key profiles. Finally, we propose an optimum strategy to mitigate the influence of the fluctuating methanol feed concentration, i.e., purposely fluctuating the anode or cathode stoichiometry. The simulation results clearly show that when a fluctuating methanol feed concentration is present, a constant cell voltage of approximately 340 mV was successfully maintained by fluctuating the cathode stoichiometry between 3.0 and 4.0.

Introduction

Pure or high-concentration methanol solution must be stored in the fuel reservoir of active-type direct methanol fuel cell (DMFC) systems to ensure high energy density. However, the methanol solution should be mixed with water before it is fed into the DMFC because the methanol oxidation reaction (MOR) at the anode requires sufficient water. More importantly, dilution of the methanol feed stream by water is key to mitigating methanol crossover toward the cathode. However, an overly low methanol feed concentration limits the methanol transport from the anode channel to the anode catalyst layer

* *Corresponding author*. Tel.: +82 32 860 7312; fax: +82 32 868 1716.
E-mail address: hcju@inha.ac.kr (H. Ju).

http://dx.doi.org/10.1016/j.ijhydene.2015.01.062

(CL), significantly increasing the anode overpotential. For stable and efficient DMFC operations, an optimum methanol feed concentration should be carefully chosen based on the DMFC design and operating conditions.

In active-type DMFC systems, outlet streams from the DMFC stack are recirculated through closed-loop control of the methanol feed concentration. The methanol concentration in the anode stream is monitored by a concentration sensor that provides feedback for the appropriate injection of additional methanol and/or water to restore the target concentration. Several types of methanol concentration sensors have been introduced in the literature to more adequately control and attain a target methanol feed concentration [1–4]. Zhao et al. [1] compared various methanol concentration sensors for DMFC applications, providing the operating principles for individual sensors, along with their advantages and disadvantages. They concluded that none of these sensors met all of the requirements for an ideal methanol concentration sensor for DMFC systems, which include wide methanol concentration ranges, high resolution and accuracy, rapid response times, long-term stability, and small sensor size. Yang et al. [2] presented a methanol sensor using Pt dots on a Nafion membrane to detect methanol concentration in real time. They fabricated the methanol sensor with H-grid type electrodes and analyzed the effects of distance and number of electrode branches. They showed that the error was maintained within 2% and can be further reduced by increasing the number of branches and decreasing the distance between electrode branches. In contrast, Ha et al. [3] proposed the sensorless control of inlet methanol concentration by estimating the rate of methanol consumption during a DMFC operation. They showed that the target concentration deviated by 20% at most over long-term DMFC operations. Chang et al. [4] developed a new sensorless control scheme for methanol supply under dynamic DMFC operations. They applied the scheme to a DVD player powered by a 40-W DMFC system and successfully demonstrated that the response time was reduced up to 5 s.

Although several sensors and methods to control methanol feed concentration have been proposed in the literature, they are not sufficiently accurate because of cell degradation and the complexity of DMFC operations. Consequently, the fluctuation in methanol feed concentration caused by inexact monitoring and control of the anode methanol flow seems inevitable in active DMFC systems. Therefore, the primary objectives of the present study are to investigate the transient response of DMFCs under fluctuating methanol feed concentrations and to suggest an operating strategy for minimizing the effects of such fluctuations. Using a one-dimensional (1-D) two-phase transient DMFC model developed in our previous studies [5–8], we conduct various transient DMFC simulations under different anode/cathode stoichiometries, cell operating temperatures, and cathode inlet humidification conditions. The model clearly addresses the influence of fluctuations in the methanol feed concentration on the cell voltage, temperature, methanol crossover, and overall cell efficiency under the specified DMFC operating conditions. Finally, based on the predicted results, we detail an effective DMFC operating strategy to reduce the effect of fluctuating methanol feed concentration.

Numerical model

Model description and assumptions

In this study, we employed the 1-D two-phase transient nonisothermal DMFC model developed in our previous studies [5–8], which was successfully validated against the experimental data measured under a wide range of cell designs and operating conditions [7]. First, the 1-D DMFC model was incorporated with a boundary condition describing methanol concentration fluctuation, then applied to the 1-D computational domain of a DMFC membrane electrode assembly (MEA) comprising diffusion layers (DLs), CLs on both the anode and cathode, and a membrane. The primary assumptions invoked in the present model are as follows:

(1) The gas phase obeys the ideal gas law, which is valid because all gases in the DMFC are maintained at high temperatures (above room temperature) and lower pressures than their respective critical pressures.
(2) The temperature gradient along the cell thickness is neglected in the 1-D model because of the very thin MEA (<1 mm) used in the DMFC.
(3) An isotropic and homogeneous porous DL is assumed, which is characterized by effective porosity and permeability.
(4) The effect of CO_2 blockage on the cell performance is negligible.
(5) Complete consumption of methanol at the cathode CL after crossing over the membrane from the anode to the cathode is assumed. This assumption is reasonable because the MOR is more facile than the oxygen reduction reaction (ORR); hence, the methanol crossing over the membrane is expected to be completely oxidized at the cathode. In addition, Wang et al. [9] experimentally found the complete oxidation of crossed-over methanol at the cathode.
(6) The electrolyte membrane is fully hydrated by the dominant liquid phase in the DMFC, which is based on the fact that an aqueous methanol solution is supplied as the fuel at the anode and significant flooding usually occurs at the cathode because of the combined effects of methanol crossover and the ORR.
(7) Complete evaporation of water during transport from the anode to the cathode is assumed, which facilitates the present analysis of coupled transient and thermal behaviors of a DMFC.
(8) The effects of O_2 and CO_2 crossover through the membrane are neglected.

Species balance equations

Because detailed descriptions of the species balance equations were previously reported by Ko et al. and Chippar et al. [5–8], only a brief description of these equations is provided here. Methanol diffusion in both the liquid and gas phases can be described by Maxwell–Stefan's multicomponent diffusion equation, in which Henry's law was applied to relate the

Please cite this article in press as: Gwak G, et al., Analyzing the effects of fluctuating methanol feed concentration in active-type direct methanol fuel cell (DMFC) systems, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.01.062