Applied Energy 129 (2014) 104–111

Contents lists available at ScienceDirect

Applied Energy

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

# Sensor-less control of the methanol concentration of direct methanol fuel cells at varying ambient temperatures

Myung-Gi An, Asad Mehmood, Heung Yong Ha *

*Energy Convergence Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea*
*Department of Energy and Environmental Engineering, Korea University of Science and Technology (UST), Yuseong-gu, Daejeon 305-333, Republic of Korea*

## HIGHLIGHTS

- A new algorithm is proposed for the sensor-less control of methanol concentration.
- Two different strategies are used depending on the ambient temperatures.
- Energy efficiency of the DMFC system has been improved by using the new algorithm.

## ARTICLE INFO

*Article history:*
Received 2 February 2014
Received in revised form 24 April 2014
Accepted 28 April 2014
Available online 22 May 2014

*Keywords:*
Direct methanol fuel cell
Sensor-less control
Methanol concentration
Stack temperature
Ambient temperature

## ABSTRACT

A new version of an algorithm is used to control the methanol concentration in the feed of DMFC systems without using methanol sensors under varying ambient temperatures. The methanol concentration is controlled indirectly by controlling the temperature of the DMFC stack, which correlates well with the methanol concentration. Depending on the ambient temperature relative to a preset reference temperature, two different strategies are used to control the stack temperature: either reducing the cooling rate of the methanol solution passing through an anode-side heat exchanger; or, lowering the pumping rate of the pure methanol to the depleted feed solution. The feasibility of the algorithm is evaluated using a DMFC system that consists of a 200 W stack and the balance of plant (BOP). The DMFC system includes a sensor-less methanol controller that is operated using a LabView system as the central processing unit. The algorithm is experimentally confirmed to precisely control the methanol concentration and the stack temperature at target values under an environment of varying ambient temperatures.

## 1. Introduction

Direct methanol fuel cells (DMFCs) continue to garner interest as a clean energy technology for powering small and portable electronic devices because of positive characteristics such as high-energy density, flexibility in power output from sub-watt to several hundred watts, and reliable operation. Over the past decade, a number of worldwide efforts have been focused on improving the performance and durability of DMFCs [1–9]. However, DMFCs still suffer from low efficiency because of poor electrode kinetics and methanol crossover from the anode to the cathode through the polymer electrolyte membrane [10,11]. The methanol crossover leads to not only fuel waste, but also mixed potential at the cathode, which adversely affects the performance and fuel efficiency [12]. The methanol crossover rate is mainly influenced by the concentration of the methanol feed at the anode and by the operating temperature of the DMFC [13]. Controlling the methanol concentration in an adequate range therefore reduces the methanol crossover under given operating conditions, and plays a critical role in stable and efficient DMFC operations. In order to achieve this goal, electronic sensors are generally installed in a feed re-circulating DMFC system to monitor and control the methanol concentration. However, the sensors are known to have many problems in terms of cost, size, durability and reliability. Zhao et al. [14] reviewed various methanol sensors for DMFCs that are generally classified into two groups: electrochemical and physical. Physical sensors are reliable and have a wide measurement range, but they are expensive and too bulky for use in portable DMFC systems. Electrochemical sensors are known to have a narrow sensing range and a slow response time due to diffusion limitations, which hampers their reliability. These also have durability issues due to a degradation of the electrolyte membranes and a deterioration of the electrodes with operating time. Some efforts have been made

---

* Corresponding author at: Energy Convergence Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea. Tel.: +82 2 958 5275; fax: +82 2 958 5229.

*E-mail address:* hyha@kist.re.kr (H.Y. Ha).

http://dx.doi.org/10.1016/j.apenergy.2014.04.100
0306-2619/

to solve the problems of electronic sensors, and, as a result, sensor-less methanol controllers have been proposed and reported by some research groups.

Several researchers have reported sensor-less methanol control using consumption equations rather than sensors to estimate the methanol concentration in the feed [13,15,16]. Chiu and Lien [13] proposed a three-dimensional measurement space (CCS) and an interpolation algorithm (ICCS) based on the constant-concentration surfaces. Once the CCS ($I$, $V$, $T$) is obtained for the known methanol concentrations in the feed, the unknown methanol concentration that corresponds to the *in situ*-measured data ($I_u$, $V_u$, $T_u$) can be estimated by interpolation. By using the ICCS, they estimated the methanol concentrations in the feed based on the current, voltage, and cell temperature of a fuel cell. Ha et al. [15] devised a sensor-less algorithm that could control the methanol concentration at a set value by supplying the same amount of methanol consumed in a DMFC system to the recirculating methanol feed solution. They built a database of methanol consumption rates that were collected under various operating conditions and utilized the database to calculate the amount of methanol needed to maintain the methanol feed concentration at a set value. Shen et al. [16] reported a real-time fuel control algorithm based on Chiu and Lien's ICCS ($I$, $V$, $T$) algorithm. They modified the ICCS algorithm by accounting for the "MEA decay" and including an *in situ* estimating method in their control program that could estimate the methanol and water consumption quantities by accumulating the operating time and the methanol and water consumption rates. The program could be used to determine the remaining amount of methanol in the operating DMFC system that could be used to control the methanol concentration by compensating for the depleted methanol feed solution. On the other hand, other studies [17–23] have reported sensor-less methods that utilized the DMFC operating characteristics as feedback parameters to control the methanol concentration in the feed. Chang et al. [17,18] reported a sensor-less algorithm that was referred to as "impulse response based on discrete-time fuel-injection" (IR-DTFI) along with a modified version that could regulate the fuel concentration in order to optimize fuel cell performance by accounting for the changes in the characteristic values of a DMFC stack, such as voltage, current, and power, during a set period of operation. They [19] also suggested an advanced version referred to as "impulse response based on current-integral and discrete-time fuel-injection" (IR-CIDTFI) algorithm that could shorten the monitoring period (5 s or less) by calculating the amount of fuel consumed during the last monitoring cycle for faster system response and greater stability. They tested the performance of IR-DTFI with a 40 W DMFC system to power portable electronics and to evaluate the effectiveness of both IR-DTFI and IR-CIDTFI algorithms from the point of operating characteristics [20,21]. Arisetty et al. [22] found that maximum voltage could be obtained by adjusting the methanol concentration in the feed under a given current density. Based on this finding, they developed an *in situ* sensor-less methodology that employed the cell voltage as the feedback to optimize the methanol concentration for maximum power density under dynamic operating conditions while maintaining a high level of fuel utilization. Lian and Yang [23] developed a sensor-less adaptive fuel concentration control (SAFCC) algorithm to regulate the methanol concentration in a suitable range by detecting transient voltage behavior under pulse-like changes in the load current. Although those sensor-less controllers are believed to be useful in controlling the methanol concentration, no controller has ever accounted for the effect of the ambient temperature surrounding a DMFC system.

Our first version of the sensor-less methanol concentration controller [15] was designed to regulate the methanol concentration in the feed by supplying an amount of pure methanol to the recirculating methanol feed solution that would be equal to the amount of methanol consumed in a DMFC system. Later, the algorithm was revised to improve its accuracy by using the stack temperature as a feedback parameter, which has a close correlation with the methanol concentration [24]. This algorithm has been further modified during this study by including the ambient temperature as a feedback parameter. Ambient temperature affects the stack temperature to allow deviation from a set value. Change in the stack temperature can be recovered by adjusting either the cooling rate of the anode heat exchanger or the pumping rate of the pure methanol to the depleted feed solution. When the ambient temperature is lower than the reference temperature (i.e., 23 °C in this study), the stack temperature decreases to below the set value because of excessive heat loss from the stack. In this case, the temperature of the circulating methanol solution can be raised by decreasing the cooling rate of the heat exchanger to compensate for the heat loss from the DMFC stack while the pumping rate of the pure methanol remains unchanged. On the other hand, when the ambient temperature is higher than the reference value, however, the heat loss from the stack is lowered and therefore the stack temperature increases above the set value. In this case, the pure methanol pumping rate can be lowered to decrease the methanol concentration in the feed, thus returning the stack temperature to the set value. The lowered methanol concentration reduces the methanol crossover rate, decreasing the heat generation at the cathode and lowering the stack temperature.

In the present study, a new version of a sensor-less methanol concentration control algorithm has been proposed based on the feedback from ambient temperatures (SLCCFA). The effects of ambient temperature on the temperature and the feed concentration of a DMFC stack are explored in detail under various operating conditions, and these are used in designing a sensor-less algorithm. The feasibility of the new sensor-less algorithm has been evaluated in terms of the methanol concentration, stack temperature and system efficiency of a 200 WDMFC system.

## 2. Experimental setup

### 2.1. Building a database of methanol consumption rates in a DMFC stack

In this control algorithm, the methanol consumption rates measured with a typical DMFC were used to calculate the amounts of pure methanol needed to compensate for the depleted feed solution under various operating conditions. The amounts of pure methanol to be pumped were determined by the experimental equations made in our earlier work [15]. The methanol consumption rates had been measured using a large-size single-cell DMFC with an active area of 150 cm$^2$ under various operating conditions by changing the output current, methanol concentration in the feed (1.3, 2.6, 3.2, and 3.8 wt.%), and cell temperature (40, 60, and 80 °C) under fixed flow rates of air (1118 ml min$^{-1}$) and methanol feed (8.78 ml min$^{-1}$) based on a 3/3 stoichiometry (O$_2$/methanol).

The total methanol consumption rate ($N_{m,t}$) in a DMFC is the sum of the methanol consumption rates by electrochemical oxidation ($N_{m,e}$) and methanol crossover ($N_{m,x}$) (Eq. (1)) [15].

$$N_{m,t} = N_{m,e} + N_{m,x} \tag{1}$$

$N_{m,e}$ was estimated based on the output current, and $N_{m,x}$ was obtained by measuring the amount of CO$_2$ at the cathode outlet that was produced by the oxidation of crossed-over methanol at the cathode. The amount of unreacted methanol that was exhausted from the cathode outlet was considered negligible because most of the crossed-over methanol was oxidized to CO$_2$ at the cathode. However, a significant amount of CO$_2$ generated