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A sensor-less methanol concentration control system based on feedback from the stack temperature

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HIGHLIGHTS

- A new sensor-less methanol control algorithm based on feedback from the stack temperature is developed.
- Feasibility of the algorithm is tested using a DMFC system with a recirculating fuel loop.
- The algorithm precisely controls the methanol concentration without the use of methanol sensors.
- The sensor-less controller shortens the time that the DMFC system requires to go from start-up to steady-state.
- This controller is effective in handling unexpected changes in the methanol concentration and stack temperature.

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ABSTRACT

A sensor-less methanol concentration control system based on feedback from the stack temperature (SLCCF) has been developed. The SLCCF algorithm is embedded into an in-house LabVIEW program that has been developed to control the methanol concentration in the feed of direct methanol fuel cells (DMFCs). This control method utilizes the close correlation between the stack temperature and the methanol concentration in the feed. Basically, the amounts of methanol to be supplied to the re-circulating feed stream are determined by estimating the methanol consumption rates under given operating conditions, which are then adjusted by a proportional–integral controller and supplied into the feed stream to maintain the stack temperature at a set value. The algorithm is designed to control the methanol concentration and the stack temperature for both start-up and normal operation processes. Feasibility tests with a 200 W-class DMFC system under various operating conditions confirm that the algorithm successfully maintains the methanol concentration in the feed as well as the stack temperature at set values, and the start-up time required for the DMFC system to reach steady-state operating conditions is reduced significantly compared with conventional sensor-less methods.

1. Introduction

Direct methanol fuel cells have been recognized as power sources with enormous potential for portable applications because of their high energy density, compact size, and long discharge time compared with rechargeable batteries [1–3]. A number of studies have already demonstrated the feasibility of DMFC systems for powering a wide range of portable applications [4–7]. Nevertheless, the successful commercialization of DMFCs requires considerable improvements in their performance and operational durability. To achieve this goal, optimization of the electrode structure, development of component materials, evaluation of the performance degradation, and mathematical modeling have been actively conducted [8–12]. In addition, concentrated methanol solutions with a content higher than 40 wt.% should be used in the feed in order to improve the energy density of DMFC systems. However, directly supplying a concentrated methanol feed to DMFC stacks can increase the methanol cross-over rates, and thus accelerate degradation phenomena [13]; therefore, a methanol feed of approximately 3 wt.% diluted with water is normally used. The unreacted methanol that exhausts out of the stack must be subsequently re-circulated to the methanol feed stream. A sophisti cated control technology is necessary in order to use a concentrated methanol solution and to re-use the unreacted methanol exhaust in re-circulating DMFC systerms.

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In general, electronic methanol sensors are utilized in the re-circulating DMFC systems to control the methanol concentration [14]. However, the installment of a methanol sensor can reduce the energy efficiency and increase the manufacturing cost of DMFC systems. In particular, consideration of the energy efficiency for portable DMFCs is critical. A simple BOP (balance of plant) is needed to reduce system weight and size as well as parasitic power losses in order to increase the energy efficiency. From this point of view, expensive methanol sensors with poor durability have a negative effect on the cost, volume and stability of DMFC systems.

As a solution, several sensor-less DMFC systems are being proposed by research groups. Chang et al. [15,16] reported that an impulse response based on a discrete-time fuel-injection (IR-DTFI) control algorithm could determine the additional injection of methanol by observing operating parameters during a set period. The same group also demonstrated an impulse response based on current-integral and discrete-time fuel-injection (IR-CIDTFI) algorithm with a 40 W DMFC system [6,17,18]. Other studies have reported the use of cell voltages and transient voltage behaviors as feedback parameters to regulate the methanol concentration [19,20]. In an earlier study, we presented an algorithm for the sensor-less control of methanol concentration (SLCC) using a database of the methanol consumption rates [21]. However, this method has few drawbacks such as longer time requirements for reaching the set methanol concentrations and malfunctions in controlling unexpected conditions such as significant variations in ambient temperatures.

In particular, none of the above methods address the start-up period of DMFC systems where methanol concentration, electric load and stack temperature vary simultaneously. Most DMFC systems use secondary batteries to warm up the stacks during the start-up period until the stack temperature reaches a set value (typically between 60 and 80 °C). However, the use of a secondary battery increases the system volume and decreases the total energy efficiency. For this reason, Chen et al. [6] used a high methanol solution of 9 wt.% (about 2.8 mol L^{-1}) to reduce the start-up time from 25 to 10 min. But this method is not suitable for use in the sensor-less DMFC systems, because a 9 wt.% methanol solution could not be duplicated *in situ* without a methanol sensor. Thus, a separate liquid tank is needed to reserve the concentrated methanol solution. Moreover, even though Chen's report suggested a method to increase the stack temperature, it gave no hint concerning how to simultaneously increase the temperature and output current of a stack at start-up. A sudden rise in the current during the start-up period could negatively influence the system durability, while a sluggish rise in the current could unnecessarily increase the time to reach target operating levels of current, methanol concentration, and stack temperature. Therefore, proper methods are required to simultaneously control the current and methanol concentration in the start-up period of DMFC systems.

In the present study, we propose a new version of a sensor-less methanol concentration control algorithm based on feedback from the stack temperature (SLCCF) to improve the accuracy of the conventional SLCC algorithm. The new algorithm includes methods to simultaneously control the output current and methanol concentration in the start-up period as well as the methanol feed concentration and stack temperature under steady-state operating conditions. In addition, proportional-integral (PI) controllers are employed to precisely control the methanol concentrations. Performance of the SLCC and SLCCF algorithms are compared in terms of the accuracy of the controls and the speeds to reach target levels of temperature and methanol concentration. In addition, the SLCCF is tested under abnormal conditions in order to assess the advantages of this control system.

2. Experimental

2.1. Configuration of a sensor-less DMFC system

In this study, the 200 W DMFC system shown in Fig. 1 was fabricated and operated to evaluate the operating characteristics of the SLCCF algorithm. The DMFC system was comprised of a methanol mixing chamber, three liquid pumps, a 200 W stack, two heat exchangers and air-blowing fans, a pure methanol reservoir, a water reservoir, a liquid-level sensor, three thermocouples (K-type), an electric load, and an air blower. The stack was assembled with 20 single cells using graphite separators with a parallel serpentine-type flow field. The membrane electrode assemblies (MEAs) used in the stack were purchased from Johnson-Matthey, Inc. Each MEA had an active area of 150 cm^2 that consisted of a Nafion 115 membrane, an anode with a 6 mg-PtRu cm^{-2} catalyst and a cathode with a 2 mg-Pt cm^{-2} catalyst. RBL488 (TDI power) provided the electric load, and was connected by a GPIB cable (National Instruments) to the main computer (SLCCF controller). Three liquid pumps were used: one (pure-methanol pump) to pump pure methanol into the methanol mixing chamber, another (main pump) to circulate a methanol feed solution along the feed recirculation loop passing through the stack, and the last (water pump) to supply condensed water from the cathode heat exchanger to the methanol mixing chamber. They were operated upon voltage signals generated by LabVIEW software and a DAQ board (National Instruments). When the level of methanol solution in the mixing chamber was lower than the preset height, the water-feed pump started supplying water from the water reservoir to the mixing chamber. There were three thermo-couples (K-type) attached to the outlet ($T_{h.out}$) of the anode heat exchanger, and the anode inlet ($T_{an.in}$) and outlet (T) of the stack to measure the temperatures of the methanol feed circulating through the fuel loop. In order to measure the methanol concentration, a methanol sensor (FC 10, ISSYS) was installed between the mixing chamber and the anode inlet of the stack, which was used for monitoring the methanol concentration rather than controlling it. The air-cooled heat exchangers were made of stainless steel and were integrated with the cooling fans. The cooling fans and a pure-methanol feed pump (FMI LAB PUMP, QB) were operated upon signals from a DC power supply (GPD-3303s, GwINSTEK) controlled by LabVIEW software.

2.2. Measurement of methanol consumption rates in a DMFC

The methanol consumption rates in the DMFC stacks were determined by the equations used in our early work [21]. Herein is a brief account of the measurement method using a large-size single DMFC with an active area of 150 cm^2. The MEAs and bipolar plates used in the single cell were the same as those of the DMFC stack. The methanol consumption rates were measured by varying the output current (through an electric load), the concentration of methanol in the feed (0.4, 0.8, 1.0, and 1.2 M (mol L^{-1})), and the cell temperature (40, 60, and 80 °C) under fixed-flow rates of air (1,118 ml min^{-1}) and methanol feed (8.78 ml min^{-1}) based on a 3/3 stoichiometry. The total methanol consumption rate ($N_{m,t}$) in the single DMFC was the sum of the methanol consumption rates ($N_{m,e}$) by electrochemical oxidation and methanol crossover ($N_{m,x}$) from anode to cathode (Eq. (1)).

$$N_{m,t} = N_{m,e} + N_{m,x} \quad (1)$$

where $N_{m,e}$ was calculated based on the output current, and $N_{m,x}$ was obtained from the amount of CO_2 produced by the oxidation of crossed-over methanol at the cathode. The amount of CO_2 was measured using a CO_2 analyzer (Vaisala GMP70) attached to the