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A novel method of methanol concentration control through feedback of the amplitudes of output voltage fluctuations for direct methanol fuel cells

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ABSTRACT

This study proposes a novel method for controlling the methanol concentration without using methanol sensors for DMFC (direct methanol fuel cell) systems that have a recycling methanol-feed loop. This method utilizes the amplitudes of output voltage fluctuations of DMFC as a feedback parameter to control the methanol concentration. The relationship between the methanol concentrations and the amplitudes of output voltage fluctuations is correlated under various operating conditions and, based on the experimental correlations, an algorithm to control the methanol concentration with no sensor is established. Feasibility tests of the algorithm have been conducted under various operating conditions including varying ambient temperature with a 200 W-class DMFC system. It is demonstrated that the sensor-less controller is able to control the methanol-feed concentration precisely and to run the DMFC systems more energy-efficiently as compared with other control systems.

1. Introduction

Fuel cells are considered as the most effective electrochemical devices that can convert chemical energy into electricity without combusting fuel [1,2]. Among various types of fuel cells, DMFCs (direct methanol fuel cells) remain attractive for portable applications because of their compact size, easy refueling, and high energy density. Performance and cost of the fuel cells, however, are major hurdles in their commercialization. Since DMFCs use much more amount of catalysts than PEMFCs (polymer electrolyte fuel cells), the cost of catalyst contributes a considerable portion of the systems. Therefore, many research groups have been developing novel electrocatalysts for improving the performance and durability [3–5] of the fuel cells. DMFCs also suffer from performance degradation due to, for example, ineffective water management [6,7] and catalyst deactivation [8]. N-doped carbon shell-coated PtFe NPs (nanoparticles) was recently reported to have an excellent long-term stability because the carbon shell prevented PtFe NPs from coalescence during fuel cell operations [3].

Direct methanol fuel cell systems generally consist of a fuel cell stack and BOP (balance-of–plant). The latter include a fuel delivery unit, an air supplying unit, an electric power control and management unit, and a system control unit. The fuel delivery unit has a function to recycle the used methanol solution that is exhausted out of DMFC stack. Before recycling the used methanol solution to the stack its methanol concentration has to be adjusted to a proper value that is determined a priori. The fuel delivery unit having a fuel recycling function play an important role in DMFC systems because it affects the size and weight, cost, operational stability, and energy efficiency of the systems [9–16]. In general, electronic methanol sensors are used in the fuel delivery units to measure and control methanol concentrations [17–23]. However, application of these sensors is limited by a narrow range of detectable concentration, low sensitivity, susceptibility to physical stimuli, and short lifetime [24,25]. In addition, they may malfunction when gas bubbles (presumably CO_2 and water vapor) in the methanol stream block the liquid-passages in the sensors. An additional plumbing and a micropump are required to circulate a part of the methanol feed

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stream through the sensors, which increases the overall size and cost, and decreases the energy efficiency due to parasitic power losses of the pump [26–28]. To solve these problems sensor-less methanol-feed concentration controllers have been developed that are inexpensive and provide a semi-permanent lifetime as compared with sensor systems. Several studies took advantages of methanol consumption equations [29–31] or mathematical models [32] to estimate the methanol concentration in the feed. Other studies [33–39] presented sensor-less controllers that used the output voltages and temperatures of fuel cells as feedback parameters. We have also presented a sensor-less methanol concentration controller that used stack temperatures as a feedback parameter [40]. Subsequently, we suggested a modified algorithm that could deal with the changes in ambient temperature [41]. This algorithm enabled an efficient sensor-less control of methanol concentration by controlling the stack temperature through adjusting either the cooling rate of the anode heat exchanger or the pumping rate of neat methanol at varying ambient temperatures.

The aforementioned methods have mostly utilized the cell temperature, voltage, or output current as reference values to estimate the methanol concentration in the recycling methanol streams. They, however, have some drawbacks such as difficulties in building databases of methanol consumption rates and establishing correlations between methanol concentrations and output voltages which may vary over time by gradual degradation of stack performance.

In this study, a novel method of sensor-less methanol concentration control is proposed, which takes advantage of the relationship between the methanol concentrations and the amplitudes of output voltage fluctuations (voltage amplitudes). The output voltages of a DMFC experience fluctuations during operation even under steady-state operating conditions because of uneven reaction rates at the electrodes that are caused by mainly formation of CO_2 slugs at the anode and water flooding at the cathode [42–46]. The CO_2 slugs and water flooding clog the pores in the electrodes and retard the access of reactants to the catalytic sites, leading to fluctuations of output voltage. Water flooding at the cathode is expected to be more influential than the CO_2 slugs at the anode. The methanol concentration in the feed affects the methanol crossover rate and thus influences water flooding at the cathode. Thereby the degree of voltage fluctuation is proportional to the methanol concentration. Lu et al. [47] showed that the cell voltage experienced sharp fluctuations due to a slug of CO_2 at the anode channels. It caused a short-lived mass transport limitation. However, this voltage oscillation was finally eliminated by a proper gas management through an optimal design of anode flow field. Du et al. [48] exhibited that the amplitudes of voltage fluctuations increased with methanol concentration under a constant load due to the reactions of the intermediate products that are formed at the cathode. According to Ren et al. [49], the methanol permeation through a polymer electrolyte membrane causes water flooding at the cathode and decreases the cathode potential in DMFCs. Abdelkareem et al. [50] exhibited that the methanol concentration had a substantial effect on the performance degradation of passive DMFCs by inducing a water flooding at the cathode. Cha et al. [51] showed that the degree of voltage fluctuation increased with time in a durability test due to increased mass transport resistances in the diffusion of oxygen into and the removal of produced water out of the cathode. Wang et al. [52] explained that the water formed at the cathode reduced the pore spaces for oxygen transport to the reaction sites as well as inactivated a part of the electrode surface electrochemically, leading to a steeper decline of the cathode potential.

It is worth emphasizing that a proper amount of water present in the DMFC cathode helps to hydrate the polymer membrane and thus increases its proton conductivity [53]. However, severe flooding should be prevented in order to avoid rapid deterioration of cathode performance [54,55]. Therefore, the excess water at the cathode has to be removed adequately or it should be controlled at an acceptable level [20,56]. From the literature mentioned above, the methanol feed concentration is estimated to be the main factor that induces voltage fluctuations by causing water flooding, mixed potential, and intermediates reactions at the cathode.

In this study, for the first time, a sensor-less methanol concentration control algorithm is presented that utilizes the amplitudes of voltage fluctuations of DMFCs as a feedback parameter. The amplitudes of the voltage fluctuations of a 200 W DMFC stack are measured under various operating conditions to estimate the effects of methanol feed concentration, stack temperature, and reactants flow rates (stoichiometry). The sensor-less algorithm is programmed and operated using a Labview software, and its feasibility is evaluated with the DMFC system.

2. Experimental

2.1. Configuration of the DMFC system

The DMFC system used in this study was comprised of a neat methanol reservoir, a methanol recycling unit, a 200 W DMFC stack, an air supplying unit, an electric load, and a system control and operation unit including a methanol concentration controller that was run by a Labview software as shown in Fig. 1. The methanol

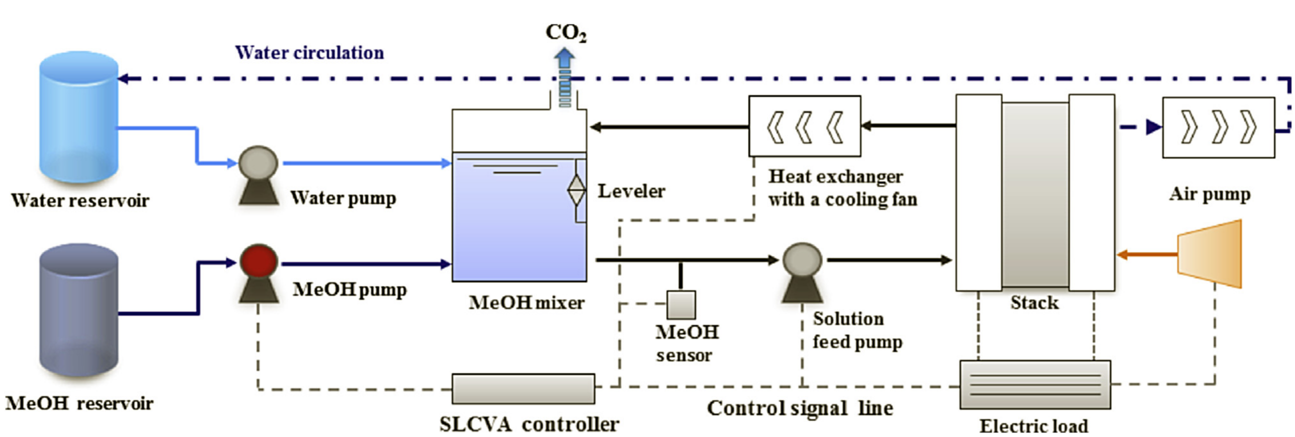

Fig. 1. Configuration of a sensor-less DMFC system with a methanol re-circulation loop.