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Dynamic response and long-term stability of a small direct methanol fuel cell stack

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ABSTRACT

This study examines the operating characteristics and durability of a small direct methanol fuel cell (DMFC) stack (volume: 39.6 cm^3). To investigate the operating characteristics in a real multi-user operating mode, various load cycles (such as gradual acceleration and deceleration), two operating modes (current mode or voltage mode) and four interrupted operating methods (load on–off, load–methanol on–off, load–air on–off, and load–methanol–air on–off) are used. The durability of the DMFC stack is examined at a constant voltage of 2.4 V (0.4 V per cell) by using the load–methanol–air on–off mode for more than 2000 h. In these tests, the DMFC stack exhibits a rapid, stable and dynamic response regardless of the load cycle and operating mode, though the stack performance and response behaviour vary with the interrupted operating modes. Among the operating modes, the air-interruption modes exhibit better stability and higher performance. Moreover, the load–methanol–air on–off mode provides the stack with good durability and a high performance in a long-term test of 2045 h.

1. Introduction

The direct methanol fuel cell (DMFC) is considered to be a promising power source for portable multi-functional electronic devices and light-duty vehicles because of its light weight, small size, high specific energy, and easy fuel storage capability [1–3]. The DMFC system, however, has several significant technical problems to be resolved, such as poor performance and methanol crossover. Accordingly, over the last decade, DMFC researchers have endeavoured to overcome the technical disadvantages through development of the proton-exchange membrane [4], the electrocatalyst [5,6], the bipolar plate [7], and the membrane electrode assembly (MEA) [8,9]. In spite of these numerous studies, several technical issues have still to be resolved for commercial applications, e.g., the durability of the fuel cell system [10] and the reliability and dynamic response in a real multi-user operating mode. These issues are of paramount importance in the design of a prototype system.

The long-term stability of MEAs is of significant concern due to degradation of cell components in either oxidizing or reducing environments that are induced by the cell reactions [11]. Many workers have examined the durability [10–17] and reliability (dynamic response) of the DMFC system [18–25]. Thomas et al. [26] studied several factors that affect the performance of DMFCs, focusing in particular on the long-term stability of the anode and the problem of methanol crossover. In that work, a life-span test at 0.4 V and 100 °C for 2000 h was conducted and showed a 12% loss in cell performance. It was suggested that the decay in the overall performance might be due to a slow drop in anode activity. Liu et al. [15] conducted a life-span test on a DMFC for 75 h at 100 mA cm^{-2} and found that 30% of the original maximum power density was lost. This performance degradation was attributed to agglomeration of the electrocatalysts and delamination of the MEA. Other researchers have also tried to determine the main parameters that govern the durability of DMFCs [27–37].

With regard to the dynamic response of DMFCs in a real multi-user operating mode, Argyropoulos et al. [18,19] emphasized not only transient operation that includes start-up and shut-down, but also the efficient transition between operating conditions for the development of engineering systems. They studied the dynamic response to consecutive changes and single-step changes in the current density and reported that the dynamic performance of the DMFC was affected by complex interactions between electrode kinetics and mass transport processes. Kallo et al. [24] observed the response of the cell voltage of a gas-feed DMFC to a step change in current density and reported the effect on the double-layer capacitance, the de-poisoning and poisoning of CO at the Pt catalyst of the anode, and the methanol crossover. Other researchers also investi-

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Table 1
Component specifications of DMFC stack.

MEA	
Membrane	Nafion 115
Catalyst of anode	PtRu/C, 1.8–2 Pt mg cm^{-2}
Catalyst of cathode	Pt/C, 1.5–1.6 Pt mg cm^{-2}
Thickness of MEA	510–530 μm
Active area of electrode	13.7 cm^2
MEA size	36 × 38 mm
Stack	
Number of cells	6 cell
Thickness of bipolar plate	1.5 mm
Size	48 × 50 × 16.5 mm
Thickness of gasket	200 μm
Total volume	39.6 cm^3

gated the dynamic behaviour of a DMFC by making a step change in the current density [20–23]. Recently, Yang and Zhao [38] developed a transient model to examine the dynamic response behaviour of a liquid-feed DMFC. The numerical results confirm that methanol permeation through the membrane produces a strong overshoot of the cathode overpotential, which is the predominant cause of voltage overshoot. By contrast, the anode overpotential is insensitive to changes in the methanol concentration and CO surface coverage in the anode catalyst layer.

Although there have been many advances in the durability and dynamic response of DMFCs, most of the reported studies have are focused on a single cell. Obviously, the results for a single cell can differ from those for a stack because each cell in the stack can exhibit different performance, fuel utility, mass transport, and methanol crossover. Thus, durability and dynamic response tests using a DMFC stack are necessary because practical systems use a stack. In addition, the operating characteristics must be examined to determine how a stack can be successfully managed in certain operating modes because this directly affects the durability of the DMFC system.

Accordingly, this investigation examines how the operating characteristics of a DMFC depend on various load cycles and operating modes; the durability with a small stack of 50.0 × 48.0 × 16.5 mm (volume: 39.6 cm^3) for a portable device is also studied.

2. Experimental

The MEA was fabricated with Nafion 115 as a proton-exchange membrane and with PtRu/C (Johnson Matthey) and Pt/C (Johnson Matthey) as electrocatalysts. For the gas-diffusion layers (GDLs) of the anode and cathode, Toray TGP060 and SGL 25BC carbon paper were used, respectively. The electrode layers were formed by applying a bar-coating method to the GDL with a catalyst slurry (comprised of Nafion ionomer and electrocatalysts). The Pt loading was 1.8–2 mg cm^{-2} for the anode and 1.5–1.6 mg cm^{-2} for the cathode.

The stack was fabricated with a small size of 50.0 × 48.0 × 16.5 mm (volume: 39.6 cm^3) for use in a digital multimedia broadcasting (DMB) phone with an output power of 5 W and a nominal voltage (2.4 V, 0.4 V per cell). The stack had six cells. Each cell had an active area of 13.7 cm^2 and internal manifolds for the supply of air and fuel. The bipolar plates, which had a thickness of 1.5 mm, were made from graphite by means of a computer numerical control lathe. A serpentine channel with two paths was used as the flow-field channel to supply air and a methanol solution to the stack. The component specifications of the DMFC stack are summarized in Table 1.

The operation characteristics of the DMFC stack were investigated with a test station (Wona Tech, Korea) equipped with an electronic load, a methanol pump, and an air pump. To evaluate the operating the characteristics of the stack in a real multi-user operating mode, various load cycles (such as gradual acceleration and deceleration), two operating modes (current or voltage mode), and four interrupted operating modes (load on–off, load–methanol on–off, load–air on–off, load–methanol–air on–off with an on-time of 30 min and an off-time of 10 s) were used.

Dynamic response tests of the stack voltage under an increasing current density step (from 0 to 200 mA cm^{-2}) are performed on two stack state (active state or inactive state). The stack is in an active state when the temperature is higher than 60 °C after consecutive operations.

In addition, to determine the optimum operating conditions for the DMFC stack, it was examined how a 1 M methanol solution (from λ = 1.5 (2.4 ml min^{-1}) to λ = 3.5 (5.3 ml min^{-1})) and air stoichiometry (λ = 1.5 (392 ml min^{-1}) to λ = 4 (1044 ml min^{-1})) affected the performance of the stack.

A durability test of the DMFC stack was performed at a constant voltage of 2.4 V (0.4 V per cell) with load–methanol–air on–off mode for more than 2000 h. After the long-term test, the changes in the stack performance were analyzed by the polarization curves, the voltage distribution of each cell, and the output power of each cell.

3. Results and discussion

The primary operating characteristics of the DMFC stack are show in Fig. 1. The DMFC stack shown in the photograph of Fig. 1(a) is designed in a U-shape, where the inlet and outlet are at the same side of the stack, so that it could be integrated with the balance-of-plant. Fig. 1(b) presents the polarization curves of the DMFC stack at different operating temperatures of 35 and 51 °C when a 1 M methanol solution (λ = 2.5) and air are supplied (λ = 3). At a low operating temperature of 35 °C, the stack has a maximum power output of 7.89 W (1.84 V at 4.29 A), a nominal power output of 6.31 W (2.4 V at 2.63 A), and a power density of 96 mW cm^{-2}. By contrast, when the stack operates at a high temperature of 51 °C, the stack performance significantly increases because the stack temperature enhances the kinetics of the electrochemical reaction [39]. At a high operating temperature of 51 °C, the stack has a maximum power output of 8.91 W (1.92 V at 4.64 A, 108 mW cm^{-2}), a nominal power output of 7.17 W (2.4 V at 2.99 A, 87 mW cm^{-2}), and a power density of more than 100 mW cm^{-2}. This stack exhibits much higher power output than the previous stack with the same electrode size and cell numbers [40], which had maximum power output of 7.63 W (1.81 V at 4.22 A, 93 mW cm^{-2}) and a nominal power output of 5.49 W (2.4 V at 2.29 A, 67 mW cm^{-2}). The results originate from improved MEA performance and component assembly method.

The voltage distribution of the six-cell stack at open-circuit voltage and a constant current of 2.8 A is given in Fig. 1(c). Each cell of the stack has a very uniform voltage distribution at 2.41 V and an open-circuit voltage of 4.99 V. This indicates that the fuel distribution inside the stack is homogeneous and the by-products of the reaction (H_2O and CO_2) are easily released. Such a uniform voltage distribution of cells in the stack would be advantageous in terms of the durability and the long-term stability of the stack. The starting opreation characteristics of the DMFC stack at a constant current of 2.82 A are presented in Fig. 1(d). The performance of the stack at the initial stage is affected by the temperature of the stack. As soon as the electric load is applied to the stack at room temperature, the voltage plunges by 2.05 V and then drastically escalates with increase in stack temperature. After 6 min, the voltage of the stack reaches 2.4 V and the output power remains between 6.74 and 6.85 W. This transient voltage possibly originates from the increased overpotential, which is attributed to an instant