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Power management of a direct methanol fuel cell system

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Abstract

The effect of discharge rate of direct methanol fuel cell (DMFC) on fuel efficiency was comparatively investigated using a DMFC single cell and a DMFC system. The results obtained from the single cell were used to model the DMFC system. Several semi-empirical equations were derived that relate discharge current, voltage, power output, energy density and fuel consumption for a nominal 25 W DMFC system. The decrease in fuel efficiency with decreased power output that is observed for the DMFC system is attributable to the increase of methanol crossover that can be observed for an individual cell. A DMFC system can achieve maximum energy density and fuel efficiency at an appropriately high level of power output.
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Keywords: DMFC; Power management; Methanol crossover; Fuel efficiency; Fuel cell

1. Introduction

With the progress in the research and development of materials and components in direct methanol fuel cells (DMFCs) [1–14], much attention has been paid to DMFC system design in recent years. A DMFC system is an electricity generator that is built by integration of multiple complex parts, including fuel cell stacks, pumps, batteries, sensors and electronic controller. For a single cell, power output capability increases with increasing methanol concentration but fuel efficiency decreases with increasing methanol concentration and decreasing current density due to the phenomenon of methanol crossover [11–14]. That and the power requirements of the balance of plat (BOP) components makes the optimum operation of a complete system difficult and non-intuitive. To assist in the optimization of system output, it was the purpose of this study to derive semi-empirical equations that could be used to relate various performance factors of a complete 25 W DMFC to that of a single cell.

In order to optimize fuel concentration for a particular power output, a DMFC system will often rely on a fuel mixer that produces a methanol–water mixture using concentrated methanol from a reservoir and the water produced at the cathodes of the fuel cell stack. Good performance of the fuel mixer is challenged by the inaccuracy of controlling methanol concentration and operating temperature. In addition to methanol concentration, there are many other complex factors that may cause fuel efficiency to decrease [15–19], which further complicates the demands on the fuel mixer. However, the effect of discharge power on fuel efficiency [20] has not received much attention in previous reports for design and operating of a DMFC system. The present article comparatively studies the effect of power management on energy output and fuel efficiency for a DMFC single cell and a DMFC system through experiment and simulation.

2. Experimental

2.1. Single cell experiment

Nafion 117 (purchased from DuPont) was used as electrolyte membrane for the DMFC single cell, which was pretreated in boiling water with 3% H_2O_2 for 2 h, then boiled in 2 M H_2SO_4 for 2 h. For each treatment the membrane was washed in de-ionized water for several times. After these treatments it was stored in water for preparation of membrane electrode assembly (MEA). The Johnson Matthey's unsupported Pt black (2 mg cm^{-2}) and Pt–Ru black (2 mg cm^{-2}) were used as catalysts for preparing electrodes. The BET surface areas of Pt

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and Pt–Ru were 27 and 60 $m^2\ g^{-1}$, respectively. The MEA was made by a hot-press at 125 °C to combine the cathode, anode, and the Nafion 117 membrane together. Then the E-Tek carbon cloths were attached to both of the cathode and the anode by a secondary hot press at 125 °C. The gas diffusion layer for the cathode had higher Teflon content than that for the anode. A single cell was fabricated by simply placing a freshly made MEA into a commercial available single cell test device (fuel cell technology) that consisted of two graphite plates. On the inner sides of the graphite plates there were two sets of micro-channels for gas and fuel flows, respectively. On the outer sides of the graphite plate, there were two cupper plates for inserting two heaters and a thermal couple, and collecting current from the fuel cell and sending current and voltage to a fuel cell test instrument through electric leads. The fuel was automatically preheated by passing through the cupper plates before entering the fuel flow channel. The active area of the DMFC single cell was 5 cm^2. The methanol flow to the anode was controlled with a HPLC pump. The anode flow was kept at 2.5 ml min^{-1} methanol solution, and cathode flow at 600 ml min^{-1} air. Methanol crossover was determined using a gravimetrical method with $Ba(OH)_2$ to precipitate CO_2 that was generated in the operation of the DMFC single cell. The CO_2 from the anode and from the cathode outlet was trapped with CO_2 getters which contained clear but saturated $Ba(OH)_2$ solution to insure precipitating the CO_2 completely. The $BaCO_3$ precipitate was separated from the liquid by a centrifuge and washed with de-ionized water, then dried at 70 °C for 20 h. After cooled on dry silicon gel in a desiccator, it was weighted delicately. The reliability of the method for quantitatively analysis of CO_2 was examined by using a CO_2 standard. The getters for CO_2 collection were calibrated by a method of a standard addition of CO_2 into the outlets of the single cell. The methanol crossover rate can be calculated with the method in literature [14]. The DMFC single cell was operated at 60 °C with 1.0 M methanol. The selected operating conditions were designed to best match the internal conditions of the DMFC system while it was in operating.

2.2. Fuel cell system and equipment

A DMFC system (SFC-A25) was purchased from SFC AG, which was designed to mix pure (100%) methanol from a fuel reservoir with the water produced in the cathode of the fuel cell stack. As the SFC-A25 had an internal lead acid battery for startup of the operation and regulation of the power output, the fuel consumption very much depends on the state of charge of this battery. The internal DMFC stack of the DMFC system was to operate at about 60 °C. The diluted fuel concentration after the fuel/water mixer was about 1.0 M, and sent to fill the fuel cell stack. The methanol concentration was controlled by a methanol sensor in the DMFC system. Even if the DMFC system was operated at room temperature (about 20 °C), the internal temperature of the DMFC stack maintained at constant (about 60 °C), except at the startup time. The specified output power of the SFC-A25 by manufacture was 25 W. The discharge voltage ranged from 11 to 14 V, depending on the output power. The air was supplied to the fuel cell by an air-compressor. Here, we define a concept of "discharge power rate" as a percentage of specified power (25 W) by the manufacture. For example, if the fuel cell system is discharged at 5, 10, 15, 20, and 25 W, the discharge power rates are 20, 40, 60, 80 and 100%, respectively.

A battery test station (model No. BT-2043, Arbin Instruments) was used for test of the DMFC system. The long term discharge performance of it was quantitatively determined under constant current discharge for three hours. The data of voltage–time curves were recorded by every 5 min. The amount of total fuel consumed was measured by the weight difference of the fuel cartridge before and after each of discharge experiments. All electrochemical measurements for DMFC system were carried out at room temperature (20 ± 1 °C).

3. Results and discussion

3.1. DMFC single cell results and analysis

Fig. 1 shows a polarization curve of a DMFC single cell at 60 °C with 1.0 M methanol as fuel and a plot of the equivalent current versus cell current for methanol migration through electrolyte membrane from the anode to the cathode. The discharge power will increase with increasing the cell current until reaching a peak value. But the rate of methanol crossover is partially mitigated by increasing cell current. At 0 discharge current there is a highest rate of methanol crossover. With increasing cell current the rate of methanol crossover decreases proportionally until reaching 0 value when the cell current is high enough. The fuel efficiency of a DMFC will be dependent on the discharge performance and the rate of methanol crossover; that is, dependent on how high the discharge voltage is and how fast the methanol migrates from the anode to the cathode.

The current potential behavior at low and middle current can be described as [21,22],

$$E_i = E_o - b\log(i_{cell}) - \frac{Ri_{cell}}{1000} \quad (1)$$

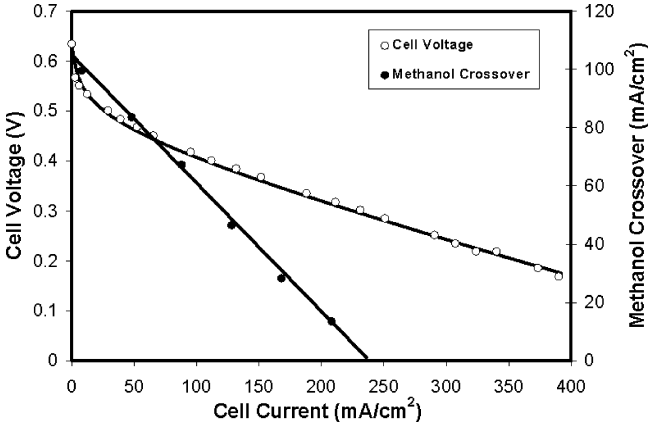

Fig. 1. Discharge polarization curve and plot of equivalent current of methanol crossover vs. cell current of a DMFC single cell using Nafion 117 as electrolyte membrane at 60 °C cell temperature with 1.0 M methanol fuel.

where E_i (V) and i_{cell} (mA cm^{-2}) are the experimentally measured cell voltage and current, E_o (V) the open circuit voltage, b (V dec^{-1}) the Tafel slope and R (Ω) is Ohmic resistance of the single cell.

The equivalent current (i_e, mA cm^{-2}) of methanol crossover can be simulated with a linear equation,

$$i_e = i_{eo} - Bi_{cell} \quad (2)$$

where i_{eo} (mA cm^{-2}) is equivalent current of methanol crossover at open circuit voltage and B is a constant.

With Eqs. (1) and (2), we can calculate the energy efficiency (η) of a DMFC single cell from the experimental discharge results.

$$\eta(\%) = \frac{i_{cell}E_i}{1.21(i_{cell} + i_e)} \times 100 \quad (3)$$

where the number 1.21 is a constant of theoretical voltage of a DMFC single cell.

Fig. 2 shows plots of energy efficiency versus discharge power and cell voltage versus discharge power obtained from the data in Fig. 1. With increasing discharge power the energy efficiency increases until reaching a peak value. On the other hand, with decreasing discharge voltage the discharge power increases until reaching a peak value. We use the dashed rectangles to mark the low power region-1 and the high power region-2, respectively, as shown in Fig. 2. In region-1 we obtain lower energy efficiency between cell voltage 0.45–0.55 V, and in region-2 we obtain higher energy efficiency between cell voltage 0.3–0.4 V. The higher energy efficiency in region-2 is attributed to a partial mitigation of methanol crossover at higher cell current and higher discharge power. Based on the single cell results, we understand that power management is necessary for a DMFC system to maximize its energy efficiency.

3.2. DMFC system results and analysis

A DMFC system was evaluated at various discharge rates by changing the discharge current. The average output power was obtained by calculations with the current data and the averaging

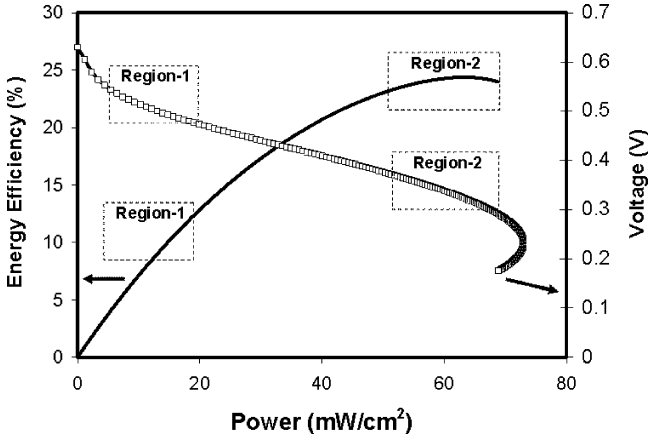

Fig. 2. Plots of energy efficiency vs. discharge power and cell voltage vs. discharge power for a DMFC single cell using Nafion 117 as electrolyte membrane at 60 °C cell temperature with 1.0 M methanol fuel.

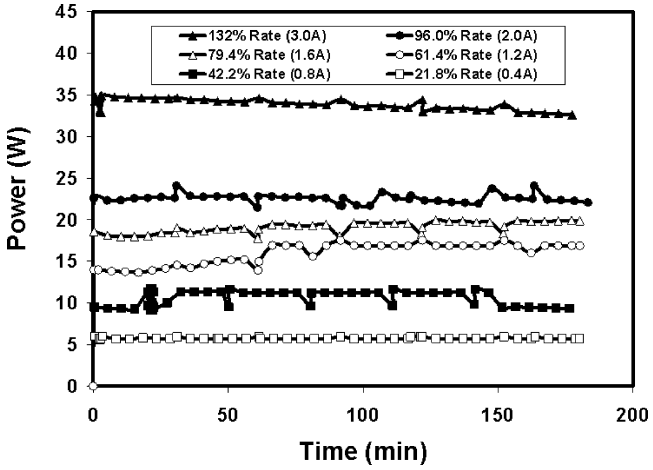

Fig. 3. Power output of a DMFC system at various discharge rates.

of voltage data. Fig. 3 shows plots of power output versus time at various discharge rates for the DMFC system. Each discharge current corresponds to a value of discharge rate. With increasing discharge current the power output becomes higher and the plateau of the power–time curve steps to a higher level in Fig. 3. The actual maximum discharge power is about 33 W, higher than the specified power 25 W by the manufacture, which results in the calculated discharge power rate reaches 132%. We will analyze the discharge performance by simulation of the relationship among current, voltage and power, and by examination of how much fuel is used for each of the discharge rates during a relative long operating term.

3.2.1. Simulation of current, voltage and power of a DMFC system

A simple statistical treatment of these data in Fig. 3 is necessary for us to quantitatively analysis of the relationship between current, voltage and power. It is well known that the electrochemical behaviors of a single fuel cell consist of three processes including electrode activation, Ohmic, and mass transfer [23–27]. In a fuel cell system the activation process occurs mainly at very small discharge current and the mass transfer process mainly at very large discharge current. Because a minimum power is needed to maintain a fuel cell system in an idling status for keeping its internal operation of air compressor, fuel pump, and for management of temperature and humidity, the electrochemical process of a DMFC system is mainly controlled by Ohmic process when the fuel cell system has a significant power output. On the other hand, a fuel cell system is also not suitable to operate at very high current because too high current will cause system-overheat. In order to avoid overheat, an upper temperature limit, and an upper current limit are set to automatically switch off the fuel cell, which implies that the DMFC system will not run under mass-transfer condition. Therefore, the discharge behavior of a DMFC system can be simplified with a linear equation under normal operating conditions (i.e., neglect the conditions of very low and very high stack current density),

$$E_V = E_V^0 - Ci \quad (4)$$

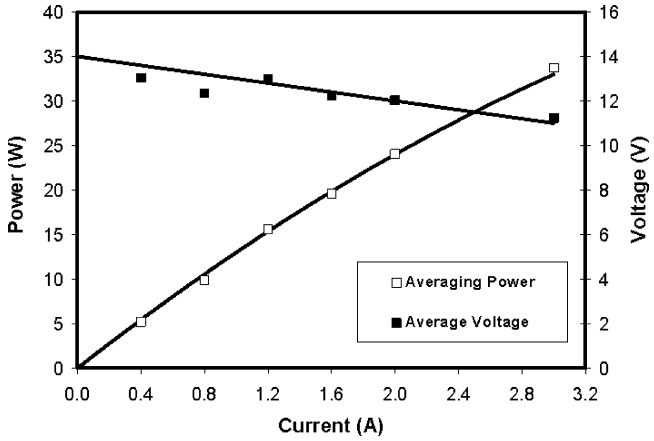

Fig. 4. Plots of power output vs. current and voltage vs. current for a DMFC system. The points are experimental data. The lines are calculated results with Eqs. (4) and (5).

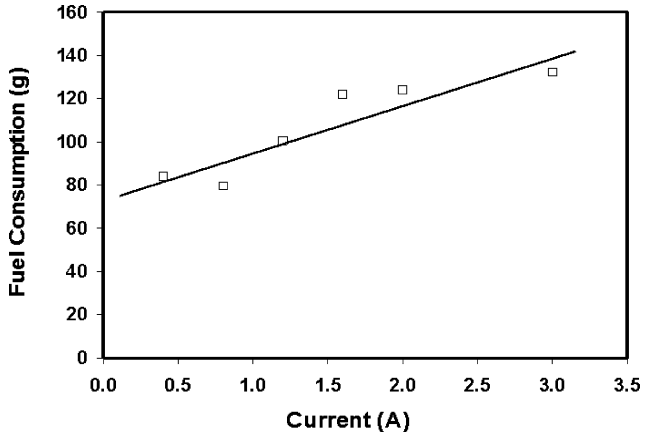

Fig. 5. Fuel consuming amount of a DMFC system for 3 h operation at different discharge current.

where E_v (V) is the discharge voltage of a DMFC system at any output current, E_V^0 (V) the discharge voltage at 0 output current, C (V A^{-1}) a constant and i (A) is discharge current of the DMFC system.

From Eq. (4), the discharge power, P_W (W), can be calculated,

$$P_W = E_V^0 i - Ci^2 \quad (5)$$

Fig. 4 shows plots of power output versus discharge current and voltage output versus discharge current for a DMFC system. Here, the points were obtained by experimental data, and the lines are the calculated data with Eqs. (4) and (5). The calculated curves fit the experimental data well. With increasing discharge current the output voltage decreases linearly, and the power increases correspondingly. The advantage of the analytical treatment is that we can find the electrochemical data without doing experiment and understand the deviation of the experimental data.

3.2.2. *Effect of fuel consumption and energy output on discharge rate*

The amount of fuel used in the fuel cell system consists of two parts, one is the electrochemically reacted fuel, and another is the un-electrochemically reacted fuel. The electrochemically reacted fuel is contributed to generate electricity, which is proportional to the discharge capacity, and in a definite time range it is proportional to the discharge current. The un-electrochemically reacted fuel is mainly contributed by the crossed over fuel through electrolyte membrane from the anode to the cathode. The crossover rate of fuel is dependent on electrolyte membrane, operating temperature, fuel concentration and discharge current. When fuel concentration and operating temperature are both relatively constant, the rate of crossed over fuel can be a constant, which is approximately proportional to discharge current. Therefore, we have a linear equation,

$$R_{cf} = R_0 + si \quad (6)$$

where R_{cf} (g h^{-1}) is the rate of fuel consuming in the DMFC systems at any discharge current, R_0 (g h^{-1}) the rate of fuel consuming at 0 discharge current and s is (g h^{-1} A^{-1}) is a constant.

Fig. 5 shows a plot of fuel consuming amount versus discharge current for a DMFC system. The rate of fuel consuming amount increases with increasing discharge current. The experimental data in Fig. 5 can be approximately treated as a straight line, and the intercept and slope of the line can be determined. Fig. 6 shows plots of fuel consuming rate versus discharge rate by calculations with Eqs. (5) and (6) and the experimental data in Fig. 5. The points and the solid line in Fig. 6 are experimental and calculated results, respectively. Even if the DMFC system is at idling condition (or no power output), it consumes about 50% of fuel in comparison with that of the DMFC working at maximum discharge rate. This result indicates that appropriately increasing discharge rate is useful to obtain higher fuel efficiency for a DMFC system.

The fuel utilization percentage (U_{fl}, %) is defined as,

$$U_{fl}(\%) = \frac{100 W_{ec}}{W_{tfl}} \quad (7)$$

where W_{ec} is the electrochemically reacted fuel and W_{tfl} is total fuel used.

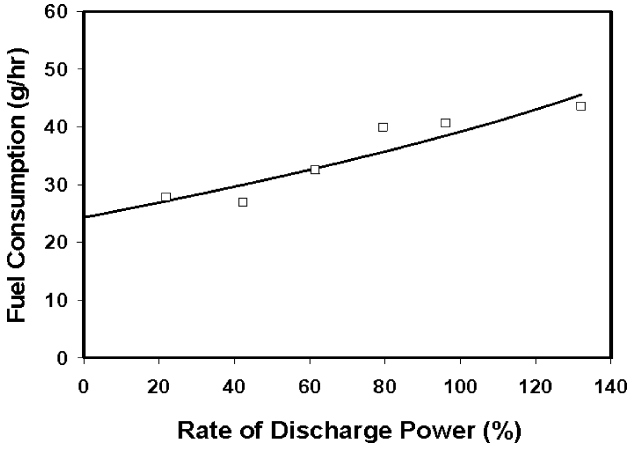

Fig. 6. Effect of fuel consumption on discharge rate for a DMFC system. The points are experimental.

The fuel efficiency % (E_{ff} %) of a DMFC system is defined as,

$$E_{ff}(\%) = \frac{100E_g}{E_{tg}} \quad (8)$$

$$E_g = \frac{1000P_W}{R_{cf}} \quad (9)$$

where E_g (W h kg^{-1}) is actual energy density, i.e., the actual generated electric energy per kilogram fuel by a DMFC system. E_{tg} (W h kg^{-1}) is the theoretical energy per kilogram of fuel.

Fig. 7 shows plots of fuel utilization % and fuel efficiency % versus discharge rate of a DMFC system, which is obtained by calculation with Eqs. (7) and (8). From the data in Fig. 7 we can find that the fuel efficiency for operating such a DMFC system at 20% power rate is only one third of that for operating of it by full power rate (100%). With increasing discharge rate both of the fuel efficiency and fuel utilization increases, because fuel crossover is partially mitigated by increasing discharge rate. The phenomenon that the value of fuel efficiency % is much smaller than that of the fuel utilization % is attributed to an energy loss caused by over potential. The theoretical voltage of a DMFC single cell is 1.21 V, but the practical operating voltage in a DMFC single cell is only 0.4 V. On the other hand, by comparison of the data of DMFC system in Fig. 7 with that of DMFC single cell in Fig. 2, the fuel efficiency of DMFC system is apparently less than that of DMFC single cell, which can be attributed to an internal consumption of electric energy by the DMFC system.

Fig. 8 shows a plot of energy density versus rate of discharge power. The points were obtained from experimental data and the line is calculated result with Eq. (9). The calculated result fits the experimental data well. This result has further demonstrated that appropriately increasing output power will result in higher energy density for a DMFC system.

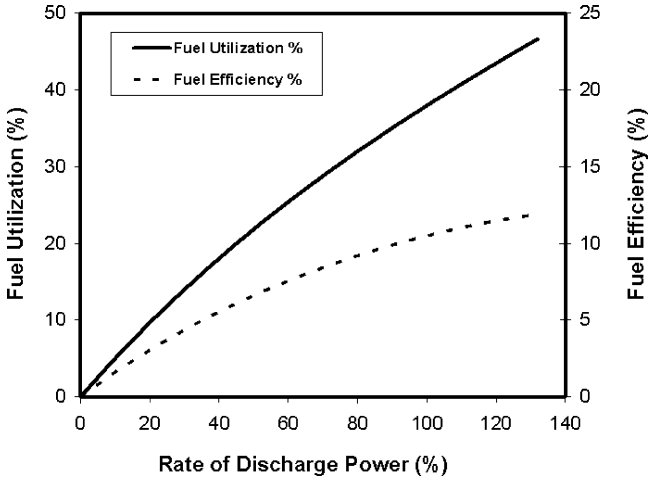

Fig. 7. Effect of fuel utilization and fuel efficiency on discharge rate for a DMFC system.

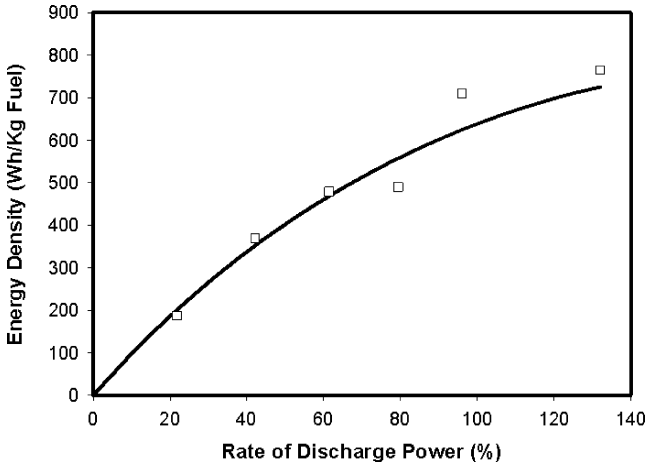

Fig. 8. Effect of energy density on discharge rate for a DMFC system. The points are experimental data. The solid line is calculated result with Eq. (9).

4. Conclusion

As shown by the experimental results from a DMFC single cell and a DMFC system, and by simulation of the relationship among current, voltage, power and fuel efficiency, the discharge rate of a DMFC system significantly affects fuel efficiency and energy density, which is attributed to significant fuel crossover in low discharge rate. Here, we need to point out that the SFC-A25 is a 4-year-old version of DMFC system. The fuel efficiency for operating such a DMFC system at 20% power rate is only one third of that for operating of it by full power rate (100%). Because of an internal consumption of electric energy by the DMFC system the fuel efficiency of a DMFC system is apparently less than that of a DMFC single cell. However, the SFC AG has recently developed a newer version of DMFC system (SFC-C20-MP), in which more digital functions and sensors are designed for optimizing the operating conditions. It is expected that a DMFC system (such as SFC-C20-MP) can achieve maximum energy density and fuel efficiency as long as its power output is adjusted at an appropriately high level. The newer version of DMFC system (SFC-C20-MP) is currently under evaluation by the US Army Research Laboratory. It is expected that much higher fuel efficiency will be obtained.

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