Heat and Mass Balance Analysis of 130-W Active-type Direct-methanol Fuel Cell

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Abstract

A “heat- and mass-balance analysis” for a direct-methanol fuel cell (DMFC) system, accounting for actual experimental data and the heat and mass transfer of the DMFC, is proposed to facilitate the usage of general spreadsheet software. The spreadsheet software enables the use of various functions on the data and visualizes the data using graphs. In addition, this application has a light computational load and is thus easy to implement in system control. The output of the analysis is the transfer of material and heat within the DMFC, as well as the heat balance and electrical efficiency of the DMFC. The analysis was verified using experimental data of the DMFC system, and the results of the verification indicated that the analysis could predict heat balance and system efficiency with accuracies of approximately 3.7% and 2.5%, respectively. Further, the analysis was used to investigate the effect of stack temperature on the electrical efficiency of the system, and the results showed that the optimum stack temperature at a system power of 130 W was 60 °C and the electrical efficiency at that temperature was 21.8% HHV.

1. Introduction

Direct-methanol fuel cells (DMFCs), which convert methanol directly into electrical energy, are expected to be utilized as small portable power sources and emergency power sources.1,2 As DMFCs have a simple system configuration and generally use an aqueous methanol solution, they offer advantages such as easy storage, handling, and refueling of methanol. However, before DMFCs become commercially viable, several problems need to be solved. Most research on DMFCs has focused on developing new electrocatalysts to facilitate the oxidation of methanol and new electrolyte materials for minimizing “methanol crossover” (MCO), a phenomenon by which methanol permeates from the anode to the cathode through the electrolyte membrane. Methanol crossover in DMFCs is among the most serious problems yet to be overcome, because it causes fuel loss and a drop in cathode potential, which leads to poor performance.3–7

While novel materials are being developed to solve these problems, there is an urgent need to understand and predict the key processes of thermal, material, and electrochemical processes occurring in a DMFC. Therefore, it is essential to develop a mathematical model for designing and optimizing a DMFC. Studies on analytical and semi-empirical models of a DMFC at the single-cell level have been reviewed by Oliveira et al.8 Although analytical models rely on several simplifying assumptions, most of them have the advantage of being able to quickly predict voltage losses in simple designs.9–12 Whereas, semi-empirical models consist of a combination of differential and algebraic equations with theoretically determined correlations and offer the advantages of having a simple structure and requiring less computational complexity involved in calculations.13–20

Several studies on system-level analyses of DMFCs have been conducted. The energy and thermal management of a DMFC system was analyzed by Doble et al., who reported that (i) the pressure and air flow rate significantly influence both the output and efficiency of the system and (ii) vaporization of water at the cathode affects the heat balance of the cell.21 Further, a mass-balance model of the components of a DMFC system was developed by Zeneth et al., who investigated the autonomy of water in a DMFC system under various operating conditions. The results of the investigation indicated that the autonomy of water is primarily dependent on three variables: ambient humidity, condenser temperature, and air flow rate.22 A one-dimensional, two-phase, multi-component DMFC model coupled with key components of a DMFC system, namely, the balance of plant (BOP), including auxiliary components such as pumps and blowers, was developed by Lee et al. They employed this model to investigate the effects of the anode inlet temperature, ambient temperature, and methanol concentration on the system behavior of a DMFC stack. The results showed that (i) the power output of the DMFC stack is improved when the anode inlet temperature is increased from approximately 70 °C to 80 °C and (ii) the higher the anode inlet temperature, the lower the power consumption of the BOP.23 A semi-empirical thermodynamic model of a DMFC system was developed by Ince et al., who investigated (i) the effects of methanol concentration, air flow, and current density on the net output and efficiency of the system, and (ii) their effect on the outlet temperature of the condenser, which determines the heat load of the condenser. The results showed that the electrical
efficiency reached its highest value (23.6 %) when the methanol concentration was 0.75 mol L⁻¹, the air flow rate was 20 mL cm⁻² min⁻¹, and the current density was 0.2 A cm⁻².²⁴

DMFC systems are typically operated under the following conditions: increased stack temperature to improve the electrocatalytic reaction, higher air volumes to prevent flooding of the cathode, and diluted methanol solutions to suppress methanol crossover.²⁵,²⁶ In a DMFC, because several processes occur simultaneously, their operating conditions affect each other. For example, a higher temperature is expected to improve both the catalytic activity of the electrode and the proton conductivity of the electrolyte membrane. However, it has negative effects such as fuel loss, voltage loss, and reduced energy density due to the increased amount of methanol crossover and water crossover. Because these characteristic changes affect the stack temperature, the cooling method for thermal management of the DMFC must be selected after understanding the contribution of each process. Therefore, conducting an analysis-driven evaluation of the system is necessary.

Analysis methods to solve these problems introduced in previous studies have mainly focused on DMFCs at the single-cell level and for design purposes, and there are relatively few reports on these systems. In addition, the computational load of the previous studies is high because of the application of advanced analysis techniques, thus implementing the analytical model in the system for field evaluation of the portable DMFC system, which is the subject of this study, outside the laboratory is challenging.

The purpose of this study is to develop a simple analysis method that is light enough to be calculated with common spreadsheet software (Excel, Microsoft) and easy to implement in the system, and to improve the efficiency of the DMFC system by identifying issues and obtaining feedback using the measurable data obtained from the system. The topics of this study are twofold: (i) to develop a simple semi-empirical analysis method that considers the coupled effect of the electrochemical reaction of the DMFC system and heat and mass transfer, and (ii) to clarify the effect of the operating conditions of the system on each process that occurs in the system.

The parameters determined at the time of operation are uniquely determined by the output; however, the stack output has multiple solutions because as it is distributed to both the system output and the auxiliary component power. Furthermore, there are various stages for determining the stack output, such as the methanol concentration, fuel circulation rate, and air flow rate, which require optimization for control. In this study, the effectiveness of the developed model was verified using measurement data of the DMFC system, and the results of estimating the effects of increasing the operating temperature of the system on its efficiency, and issues resulting from that temperature increase, have been introduced.

2. Experimental

2.1 Overview of DMFC system

The configuration of the DMFC system is shown in Fig. 1. In this system, an aqueous solution of diluted methanol was supplied to the anode side of the stack, and air was supplied to the cathode side at the desired values. The aqueous methanol solution was prepared by mixing condensed water via the condenser of the cathode side outlet and methanol from the fuel cartridge in a mixing tank and then adjusting the concentration to the desired value using a concentration sensor. Further, a diaphragm pump (FMM20, KNF) was used to pump fuel from the cartridge, while the concentration-adjusted fuel was supplied from the mixing tank to the anode side of the stack using a circulation pump (7038, NAMIKI). The supplied methanol solution reacts on the anode side of the stack to produce carbon dioxide, and subsequently, the unreacted and partially reacted methanol solution with carbon dioxide was circulated back to the mixing tank.

Moreover, air containing N₂, O₂, and H₂O(g) as the primary components was supplied to the cathode side of the stack through a filter by an air supply fan (TF037B, NIDEC Copal Electronics). After the reaction on the cathode side of the stack, the unreacted O₂ and water vapor produced by the reaction were transported to the mixing tank through the condenser, and the gas components were discharged into the atmosphere. In addition to the water generated by the reaction, the cathode side also includes the water generated due to methanol oxidation in the cathode (MOC) by methanol crossover and water crossover (WCO), owing to which the water permeates from the anode to the cathode through the electrolyte membrane by electro-osmotic drag. In addition, the crossover results in deviations from stoichiometry, and consequently extra heat is generated. However, assuming that the water is produced as a gas, the vaporization heat of this water can be used to cool the stack.

The DMFC stack comprised end plates (polyphenylene sulfide), current-collector plates (Au-coated Ti), gaskets (VMQ), carbon bipolar plates with channels, and membrane-electrode assemblies

![Figure 1. Schematic of an active DMFC system.](image-url)
Further, the MEA comprised an electrolyte membrane (DE2020CS, thickness: 50 µm, DuPont), an anode catalytic electrode (TEC81E81, Tanaka), a cathode catalytic electrode (TEC10E70TPM, Tanaka), and a diffusion layer (TGP-H-60, Toray), with an electrode area of 75.26 cm². The bipolar plates were surface treated to suppress the influence of residual water on the cathode side for stable power generation during long operation of the stack. A 51-cell stack was assembled using these components. The external appearance of the prototype DMFC system is shown in Fig. 2.

2.2 Analysis procedure

Figure 3 shows the analysis procedure employed in this study, which was conducted following the process sequence of setting initial conditions, mass transport, heat transport, condenser, convergence decision, and performance of the DMFC. The external appearance of the prototype DMFC system is shown in Fig. 2.

The solutions obtained in the convergence calculation are cell voltage, anode inlet and outlet temperatures, the cathode inlet temperature and humidity, the stack temperature under steady-state operation, the anode inlet and outlet compositions (gas–liquid), and condensate volume by the condenser, as described below. Although the water transferred to the cathode by water crossover does not change chemically, it is assumed that the water generated by power generation and MOC and the water that reaches the cathode side by water crossover are all discharged as water vapor until the saturated water vapor pressure is attained.

The consumption and production amounts of each component in the fuel cell stack are expressed as follows:

Anode: \( \text{CH}_3\text{OH(liq)} + \text{H}_2\text{O(liq)} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \)

Cathode: \( 6\text{H}^+ + 6\text{e}^- + 1.5 \text{O}_2 \rightarrow 3\text{H}_2\text{O(gas)} \)

Cathode (MOC): \( \text{CH}_3\text{OH(liq)} + 1.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O(gas)} \)

The consumption and production amounts of each component in the fuel cell stack are expressed as follows:

Methanol consumption associated with anodic reaction, \( \dot{m}_{\text{an,cons,M}} \) (g s\(^{-1}\)):

\[ \dot{m}_{\text{an,cons,M}} = M_{\text{M}} A_{\text{cell}} I/(6F) \]  

Water consumption associated with anodic reaction, \( \dot{m}_{\text{an,cons,H}_2\text{O}} \) (g s\(^{-1}\)):

\[ \dot{m}_{\text{an,cons,H}_2\text{O}} = M_{\text{H}_2\text{O}} A_{\text{cell}} I/(6F) \]

Amount of CO\(_2\) produced by the anodic reaction, \( \dot{m}_{\text{an,gen,CO}_2} \) (g s\(^{-1}\)):

\[ \dot{m}_{\text{an,gen,CO}_2} = M_{\text{CO}_2} A_{\text{cell}} I/(6F) \]

Oxygen consumption associated with cathodic reaction, \( \dot{m}_{\text{ca,cons,O}_2} \) (g s\(^{-1}\)):

\[ \dot{m}_{\text{ca,cons,O}_2} = 1.5M_{\text{O}_2} A_{\text{cell}} I/(6F) \]

Amount of water generated by cathode reaction, \( \dot{m}_{\text{ca,gen,H}_2\text{O}} \) (g s\(^{-1}\)):

\[ \dot{m}_{\text{ca,gen,H}_2\text{O}} = 3M_{\text{H}_2\text{O}} A_{\text{cell}} I/(6F) \]
methanol consumption on the anode side due to crossover, $n_{{\text{cross,an,cons,M}}}^{\text{cross}}$ (g s$^{-1}$):

$$n_{{\text{cross,an,cons,M}}}^{\text{cross}} = k_{{\text{cross}}}A_{\text{cell}}$$  \hspace{1cm} (6)

and the amount of methanol produced on the cathode side due to crossover, $n_{{\text{cross,ca,gen,M}}}^{\text{cross}}$ (g s$^{-1}$):

$$n_{{\text{cross,ca,gen,M}}}^{\text{cross}} = (1 - \alpha)n_{{\text{cross,an,cons,M}}}^{\text{cross}}$$  \hspace{1cm} (7)

Here, $\alpha$ is the rate (%) at which methanol transferred to the cathode by methanol crossover is oxidized. In this study, based on the results of elemental tests with a single cell, it is assumed that 91% of the methanol transferred to the cathode owing to methanol crossover underwent an oxidation reaction while the remaining 9% evaporated without any reaction and was discharged from the cathode.

Methanol consumption on the cathode side due to crossover, $n_{{\text{cross,ca,cons,M}}}^{\text{cross}}$ (g s$^{-1}$):

$$n_{{\text{cross,ca,cons,M}}}^{\text{cross}} = \alpha n_{{\text{cross,an,cons,M}}}^{\text{cross}}$$  \hspace{1cm} (8)

amount of CO$_2$ produced on the cathode side by crossover, $n_{{\text{cross,ca,gen,CO}_2}}$ (g s$^{-1}$):

$$n_{{\text{cross,ca,gen,CO}_2}} = n_{{\text{cross,ca,gen,M}}}^{\text{cross}} \frac{M_{\text{CO}_2}}{M_M}$$  \hspace{1cm} (9)

oxygen consumption due to crossover, $n_{{\text{cross,ca,cons,O}_2}}$ (g s$^{-1}$):

$$n_{{\text{cross,ca,cons,O}_2}} = n_{{\text{cross,ca,cons,M}}}^{\text{cross}} \frac{1.5M_{\text{O}_2}}{M_M}$$  \hspace{1cm} (10)

amount of water produced by crossover, $n_{{\text{cross,ca,gen,H}_2O}}$ (g s$^{-1}$):

$$n_{{\text{cross,ca,gen,H}_2O}} = n_{{\text{cross,ca,cons,M}}}^{\text{cross}} \frac{2M_{\text{H}_2O}}{M_M}$$  \hspace{1cm} (11)

Regarding the methanol crossover coefficient, $k_{{\text{cross}}}$ (µg cm$^{-2}$s$^{-1}$), the following relational expression based on the activation energy equation was derived from the experimental values for a single cell using multiple regression analysis:

$$k_{{\text{cross}}} = 10^{-6} \beta_1 \exp \left( \frac{\beta_2}{T_{\text{STK}}} \right) \left( \beta_3 T_{\text{STK}} + \beta_4 I + \beta_5 \right)$$  \hspace{1cm} (12)

coefficients $\beta_1$ to $\beta_5$ are given as follows:

$$\beta_1 = 13.126, \quad \beta_2 = -1121, \quad \beta_3 = 0.135,$$

$$\beta_4 = 0.473, \quad \beta_5 = 0.0015, \quad \text{and} \quad \beta_6 = 41.947$$

In this study, it is assumed that (i) the amount of water crossover is obtained by subtracting the water consumption due to power generation from the water consumption on the anode side and (ii) the entire amount of the water crossover moves to the cathode through the electrolyte membrane. The calculation method employed was as follows:

- The amount of water loss in the cartridge due to power generation was measured.
- The relative humidity on the cathode side was calculated from the measured amount of water loss and stack temperature.
- Considering the calculated relative humidity as the target parameter, the water amount was calculated such that the water crossover amount approached this relative humidity.

The mass balance can be calculated using Eqs. 1–12. If an aqueous methanol solution with the same concentration as that consumed by the system operation is fed into the fuel cartridge shown in Fig. 1, the mass balance is balanced. In this study, the concentration of the aqueous methanol solution in the fuel cartridge was set to 60 wt%. The shortage of water was reused by condensing water vapor in the air discharged from the cathode outlet.

The amount of water recovered by the condenser, $n_{{\text{cond,gen,out,H}_2O(\text{liq})}}$ (g s$^{-1}$), is expressed as:

$$n_{{\text{cond,gen,out,H}_2O(\text{liq})}} = \left\{ \frac{N_{\text{ca,out,H}_2O}}{1 - X(T_{\text{cond,out}})} \right\} M_{\text{H}_2O}$$  \hspace{1cm} (13)

where $N_{\text{ca,out,H}_2O}$, $N_{\text{ca,out,N}_2}$, $N_{\text{ca,out,O}_2}$, $N_{\text{ca,out,CO}_2}$, and $N_{\text{ca,out,M}}$ denote the flow rates in air at the cathode outlet (mol s$^{-1}$) in the case of water, nitrogen, oxygen, carbon dioxide, and methanol, respectively. Further, $X(T_{\text{cond,out}})$ and $T_{\text{cond,out}}$ denote the percentage of saturated water vapor at the condenser outlet temperature (°C) and condenser outlet temperature (K), respectively. The amount of water to be recovered to balance the mass balance was calculated using Eq. 13. The target outlet temperature of the condenser can be obtained by determining the water-recovery amount to balance the amount of water consumed and the sum of the amount of water that can be supplied from the cartridge, the amount of water that is discharged from the cathode outlet side (without evaporation above the saturated water-vapor concentration), and the amount of water recovered.

2.4 Heat transport

Because the purpose of this study is to analyze the heat balance of the stack under different stack operating temperatures, the heat of reaction is considered as a function of temperature. The constant-pressure specific heat used in the calculations was approximated using the following polynomial equation:

$$C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^3$$  \hspace{1cm} (14)

where $C_p$ and $T$ denote the constant-pressure specific heat (J mol$^{-1}$ K$^{-1}$) and temperature (K), respectively. The specific-heat coefficients $a$, $b$, $c$, and $d$ are listed in Table 1.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$  \hspace{1cm} (15)

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$  \hspace{1cm} (16)

| Substance | $a$ / J mol$^{-1}$ K$^{-1}$ | $b$ / J mol$^{-1}$ | $c$ / J mol$^{-1}$ | $d$ / J mol$^{-1}$ |
|-----------|-----------------|----------------|-----------------|-----------------|
| N$_2$     | 28.901          | $-1.6 \times 10^{-3}$ | $8.1 \times 10^{-6}$ | $-2.9 \times 10^{-9}$ |
| O$_2$     | 25.477          | $1.5 \times 10^{-2}$ | $-7.2 \times 10^{-6}$ | $1.3 \times 10^{-9}$ |
| CO$_2$    | 22.257          | $6.0 \times 10^{-2}$ | $-3.5 \times 10^{-5}$ | $7.5 \times 10^{-9}$ |
| H$_2$O    | 32.238          | $1.9 \times 10^{-3}$ | $1.1 \times 10^{-5}$ | $-3.6 \times 10^{-9}$ |
| CH$_3$OH (liq.) | $-152.84$ | $2.293$ | $-8.1 \times 10^{-3}$ | $1.0 \times 10^{-5}$ |
| CH$_3$OH (gas) | $20.658$ | $7.1 \times 10^{-2}$ | $2.3 \times 10^{-5}$ | $-2.7 \times 10^{-8}$ |

| Substance | $H^0$ / kJ mol$^{-1}$ | $S^0$ / J mol$^{-1}$ K$^{-1}$ |
|-----------|-----------------|----------------|
| CO$_2$ (gas) | $-393.8$ | $213.8$ |
| H$_2$O (liq.) | $-285.8$ | $69.9$ |
| H$_2$O (gas) | $-242.0$ | $188.8$ |
| CH$_3$OH (liq.) | $-238.8$ | $127.2$ |
| CH$_3$OH (gas) | $-201.4$ | $239.9$ |
Three possible endothermic processes can occur in the stack. Further, the generated heat associated with the generation of the constant-pressure specific heat expressed as Eq. 15. Further, the in Fig. 4, which confirms that the calculation results (‘cal.’) are consistent with the reference values.31

The models targeting heat transfer are as follows: (i) the reaction-heat model of the stack, (ii) the heat-dissipation model of the stack, (iii) the cooling model for the fluid on the anode side, (iv) the cooling model for the fluid on the cathode side, and (v) the condenser model. In this study, the following conditions were assumed:

- Atmospheric pressure is 1 atm.
- All gas components are ideal gases.
- Air in the atmosphere is composed of nitrogen, oxygen, and water vapor only at a nitrogen to oxygen ratio (N₂ : O₂) of 78.25 : 20.74.
- Ambient temperature is 25 °C at 40 % RH.

2.4.1 Reaction-heat model of the stack

Heat generation in the stack includes heat generation owing to power generation and crossover. The total amount of heat generation \( Q_{\text{total}} \) (W) is expressed as:

\[
Q_{\text{total}} = Q_1 + Q_2
\]

Further, the generated heat associated with the generation of electricity, \( Q_1 \) (W), is obtained by subtracting the generated electricity from the amount of methanol consumed (Eq. 1) multiplied by enthalpy change \( -\Delta H(T) \) at stack temperature \( T_{\text{STK}} \) as follows:

\[
Q_1 = -\Delta H(T) m_{\text{an,cons,M}} - IAV_{\text{cell}}(T)n_{\text{cell}}
\]

where \( I, A, V_{\text{cell}}(T), \) and \( n_{\text{cell}} \) denote the current density, electrode area, cell voltage, and number of cells in the stack, respectively. The generated heat due to crossover, \( Q_2 \) (W), is given by the amount of crossover methanol and combustion on the cathode, thus, it is the amount obtained on multiplying Eq. 6 with \( -\Delta H(T) \) as follows:

\[
Q_2 = -\Delta H(T) m_{\text{an,cons,M}}^{\text{cross}}
\]

Three possible endothermic processes can occur in the stack.

i. Latent heat absorbed when unreacted water in the carbon-dioxide gas produced by the reaction on the anode side evaporates.

The heat of vaporization of water and methanol was calculated using an approximate expression with stack temperature \( T_{\text{STK}} \) as a parameter as follows:32

\[
q_{\text{H,O}} = 3147.3 - 2.3668T_{\text{STK}}
\]

heat of vaporization of methanol, \( q_m \) (kJ kg⁻¹):

\[
q_m = 1088.79 \left( \frac{512.55 - T_{\text{STK}}}{174.7} \right)^{0.4}
\]

Further, for the calculation of the latent heat of vaporization \( Q_2 \) (W), the determined amount of water vapor was compared with the amount of saturated water vapor at stack temperature \( T \) under the assumption that all the water generated on the cathode side evaporates due to reaction and WCO. Subsequently, \( Q_2 \) was calculated from the following equation as the amount of water vapor that contributes to the latent heat until the saturated water vapor amount is reached:

\[
Q_2 = q_{\text{H,O}} \left( \frac{X(T)}{1 - X(T)} \right) \left( N_{\text{ca,out,N}_2} + N_{\text{ca,out,O}_2} + N_{\text{ca,out,CO}_2} \right. \\
\left. + N_{\text{ca,out,M}} - N_{\text{ca,in,H}_2O} \right) M_{\text{H,O}}
\]

where \( N_{\text{ca,out,N}_2}, N_{\text{ca,out,O}_2}, N_{\text{ca,out,CO}_2}, N_{\text{ca,out,M}} \), denote the flow rates in the air on the stack-cathode outlet side (mol s⁻¹) in the case of nitrogen, oxygen, carbon-dioxide, methanol, respectively, and \( N_{\text{ca,in,H}_2O} \) denotes water-vapor flow rate in air on the stack-cathode inlet side (mol s⁻¹). Further, \( X(T) \) is the percentage of saturated water vapor at temperature \( T \) (vol%).

The latent heat of vaporization of methanol \( Q_4 \) (W) was calculated by multiplying Eqs. 22 and 7 as follows:

\[
Q_4 = q_m m_{\text{an,gen,M}}^{\text{cross}}
\]

The latent heat of vaporization \( Q_5 \) (W) on the anode side is calculated by the following equation under the assumption that at stack temperature \( T \), water evaporates to form saturated water vapor in the carbon dioxide gas generated on the anode side:

\[
Q_5 = q_{\text{H,O}} \left( \frac{X(T)}{1 - X(T)} \right) m_{\text{an,gen,CO}_2} M_{\text{CO}_2}
\]

2.4.2 Heat-dissipation algorithm of the stack

To calculate the amount of heat released from the stack surface, it is necessary to know the heat transfer coefficient under natural convection conditions. However, to obtain the coefficient, the natural heat dissipation (convection) characteristics of the stack needs to be measured. Accordingly, in this study, the heat-dissipation algorithm of the stack was simplified by setting the following preconditions:

- The stack shape is approximated as a rectangular parallelepiped with dimensions of 80 (W) × 145 (D) × 146 (H) (mm).
- The stack has six heat-dissipation surfaces.
- The heat dissipation of the stack is not affected by the surroundings (such as auxiliary equipment).
- The heat-transfer coefficient was assumed to be constant at a value of 5 W m⁻² K⁻¹.

The heat transfer coefficient was applied to the value obtained by measuring the heat dissipation characteristics under natural convection conditions by elemental experiments using a heat generating simulated block with a known heat capacity and a similar shape to the DMFC stack.

Under the above conditions, the amount of heat released from the stack surface \( Q_{\text{STK}} \) (W) is expressed as:
where $S$, $T_{STK}$, and $T_i$ denote the heat-dissipation area of face $k$ of the stack ($m^2$), stack temperature ($K$), and ambient temperature ($K$), respectively.

2.4.3 Model of cooling by fluid on the anode side

The heat extracted from the anode side was obtained by adding the heat of vaporization and the heat of condensation of the liquid and gas phases, respectively. The anode-cooling amount $Q_{an}$ (W) is therefore expressed as follows:

$$Q_{an} = Q_{an(liq)} + Q_{an(gas)}$$

(27)

The amount of cooling on the anode side due to the liquid phase, $Q_{an(liq)}$ (W), can be obtained from the difference in sensible heat at the stack inlets and outlets and the fuel flow rate. The specific heat coefficient $C_p$ in Eq. 14 is calculated from the concentration of methanol supplied to the stack, as follows:

$$Q_{an(liq)} = C_p \cdot an(out) \cdot T_{an(out)} \cdot m_{fuel, an(out)}$$

(28)

fuel flow rate on stack-anode inlet side, $m_{fuel, an(in)}$ (g s$^{-1}$).

$$m_{fuel, an(in)} = \frac{N_{an,in,M} \cdot M_{an} + N_{an,in,H2O} \cdot M_{H2O}}{C_p \cdot an(in)} (g s^{-1})$$

(29)

where $C_p$, $an(in)$, $T_{an(in)}$, $N_{an,in,M}$, $N_{an,in,H2O}$, $M_{an}$, and $N_{an,in,H2O}$ denote the specific heats of the fuel on the stack-anode inlet side (kJ kg$^{-1}$ K$^{-1}$), specific heat of the fuel on the stack-anode inlet side (kJ kg$^{-1}$ K$^{-1}$), stack-anode outlet temperature ($K$), stack-anode inlet temperature ($K$), methanol flow rate in the fuel on the stack-anode inlet side (mol s$^{-1}$), water flow rate in the fuel on the stack-anode inlet side (mol s$^{-1}$), methanol flow rate in the fuel on the stack-anode outlet side (mol s$^{-1}$), and water flow rate in the fuel on the stack-anode outlet side (mol s$^{-1}$), respectively.

The gas-phase components discharged from the anode outlet were carbon dioxide and water vapor produced as a result of the reaction. Consequently, the cooling amount of the anode side by the gas phase, $Q_{an(gas)}$ (W), can therefore be obtained as follows:

$$Q_{an(gas)} = C_p \cdot an(out) \cdot T_{an(out)} \cdot m_{fuel, an(out)}$$

(30)

where $C_p$, $an(out)$, $T_{an(out)}$, $N_{an,out,M}$, $N_{an,out,H2O}$, $M_{an}$, and $N_{an,out,H2O}$ denote the specific heats of the fuel on the stack-anode outlet side (kJ kg$^{-1}$ K$^{-1}$), specific heat of the fuel on the stack-anode outlet side (kJ kg$^{-1}$ K$^{-1}$), stack-anode outlet temperature ($K$), stack-anode inlet temperature ($K$), methanol flow rate in the fuel on the stack-anode outlet side (mol s$^{-1}$), water flow rate in the fuel on the stack-anode outlet side (mol s$^{-1}$), respectively.

2.4.4 Model of cooling by fluid on the cathode side

The heat eliminated from the cathode side is determined by adding the heat of the liquid and gas phases, as in the case of the anode side. The cathode-cooling amount $Q_{ca}$ (W) is expressed as follows:

$$Q_{ca} = Q_{ca(liq)} + Q_{ca(gas)}$$

(31)

Further, similar to the anode-side cooling amount, the cathode-side cooling amount is calculated from the difference in sensible heat at the stack inlet and outlet and the air flow rate.

The air composition at the cathode outlet can be calculated using Eqs. 4, 5, 7, 9, 10, and 11 and the actual data on fuel and water consumption as follows:

cathode cooling amount, $Q_{ca(gas)}$ (W):

$$Q_{ca(gas)} = C_p \cdot ca(out) \cdot T_{ca(out)} \cdot m_{ca(out)}$$

(32)

air flow rate on the stack-cathode inlet side, $m_{ca(in)}$ (g s$^{-1}$):

$$m_{ca(in)} = N_{ca,in,N} \cdot M_N + N_{ca,in,O} \cdot M_O + N_{ca,in,H2O} \cdot M_{H2O}$$

(33)

air flow rate on the stack-cathode outlet side, $m_{ca(out)}$ (g s$^{-1}$):

$$m_{ca(out)} = N_{ca,out,N} \cdot M_N + N_{ca,out,O} \cdot M_O + N_{ca,out,H2O} \cdot M_{H2O}$$

(34)

liquid-phase cathode cooling, $Q_{ca(liq)}$ (W):

$$Q_{ca(liq)} = C_p \cdot ca(out) \cdot H2O(liq) \cdot T_{ca(out)} \cdot N_{ca,out,H2O} \cdot M_{H2O}$$

(35)

where $C_p$, $ca(out)$, $H2O(liq)$, $T_{ca(out)}$, and $N_{ca,out,H2O}$ denote the specific heat of water on the stack-cathode outlet side (kJ kg$^{-1}$ K$^{-1}$), specific heat of water on the stack-cathode outlet side (kJ kg$^{-1}$ K$^{-1}$), specific heat of water (liquid phase) on the stack-cathode outlet side (kJ kg$^{-1}$ K$^{-1}$), stack-cathode outlet temperature ($K$), stack-cathode inlet temperature ($K$), and stack-cathode outlet side water (liquid phase) flow rate (mol s$^{-1}$), respectively.

2.4.5 Model of condenser

Thermal changes in the condenser include sensible heat in the gas and liquid phases and latent heat due to condensation. As a precondition, the inlet temperature of the condenser was assumed to be equal to the temperature at the cathode outlet side of the stack. Consequently, the generated heat $Q_{cond}$ (W) required for water recovery is expressed as:

$$Q_{cond} = Q_{cond(gas)} + Q_{cond(liq)} + Q_{cond(lat)}$$

(36)

where $Q_{cond(gas)}$ and $Q_{cond(liq)}$ denote the sensible heat of air on the inlet side of the condenser and the sensible heat of air on the outlet side of the condenser, respectively.

The latent heat of the liquid phase $Q_{cond(lat)}$ (W) can be obtained in manner similar to that as the sensible heat of the gas phase as follows:

$$Q_{cond(lat)} = C_p \cdot cond(out) \cdot T_{cond(out)} \cdot m_{cond(out)}$$

(37)

where $C_p$, $cond(out)$, $T_{cond(out)}$, and $m_{cond(out)}$ denote the specific heat of air on the outlet side of the condenser (kJ kg$^{-1}$ K$^{-1}$), specific heat of air on the inlet side of the condenser (i.e., outlet side of the stack) (kJ kg$^{-1}$ K$^{-1}$), temperature on the outlet side of the condenser ($K$), temperature on the inlet side of the condenser ($K$), and air flow rate on the outlet side of the condenser (g s$^{-1}$), respectively.

The latent heat of the liquid phase $Q_{cond(lat)}$ (W) can be obtained in manner similar to that as the sensible heat of the gas phase as follows:

$$Q_{cond(lat)} = C_p \cdot cond(out) \cdot H2O(liq) \cdot T_{cond(out)} \cdot m_{cond(out)} \cdot H2O$$

(38)

where $C_p$, $cond(out)$, $H2O(liq)$, $T_{cond(out)}$, and $m_{cond(out)}$ denote the specific heat of water (liquid phase) on the outlet side of the condenser (kJ kg$^{-1}$ K$^{-1}$), specific heat of water (liquid phase) on the inlet side of the condenser (kJ kg$^{-1}$ K$^{-1}$), water (liquid phase) flow rate (g s$^{-1}$) on the outlet side of the condenser, and water (liquid phase) flow rate (g s$^{-1}$) on the inlet side of the condenser, respectively.

The latent heat of condensate is calculated by multiplying the amount of condensed water cooled by the condenser using Eq. 21, as follows:

$$Q_{cond(lat)} = \phi_{H2O} \left( N_{cond(out),N} \cdot M_N + N_{cond(out),O} \cdot M_O + N_{cond(out),H2O} \cdot M_{H2O} \right)$$

(39)

where $N_{cond(out),N}$, $N_{cond(out),O}$, $N_{cond(out),CO2}$, and $N_{cond(out),H2O}$ denote the flow rates in air on the outlet side of the condenser (mol s$^{-1}$) in the case of nitrogen, oxygen, carbon dioxide, and methanol, respectively, and $N_{cond(out),H2O}$ denotes water vapor flow rate in air on the inlet side of the condenser (stack-cathode outlet side) (mol s$^{-1}$).

2.5 DMFC model

Because the DMFC model assumes steady-state analysis, to maintain a constant DMFC output, the methanol concentration, fuel flow rate, air flow rate, stack temperature, anode inlet and outlet...
temperatures, cathode inlet and outlet temperatures, and condenser outlet temperature are considered as input parameters.

The conditions assumed were an electrode area of 75.26 cm² and a number of cells of 51. Regarding the stack output, considering the auxiliary power (BOP) power, the current density was adjusted such that the system output would be 130 W. Moreover, as the methanol concentration was system-controlled at 3 wt%, in this study, it was set to a fixed value.

Further, for the cell performance, the current–voltage curve data of a single cell at each temperature was used as a quadratic multiterm approximation. The electrode area of the MEA used in the single cell was 25 cm² and the current density–voltage characteristics were performed at different current densities ranging from 0.0 to 0.5 A cm⁻², with step-size of 0.025 A cm⁻². Further, a 3 wt% methanol solution was fed to the anode side with a flow rate of 5.6 mL min⁻¹, whereas a 40% RH humidified air at ambient pressure was fed to the cathode side at a flow rate of 850 mL min⁻¹. In addition, the cell temperature was set in the range of 60–90°C.

2.6 Performance of DMFC system

The performance of the DMFC system was evaluated by measuring the consumption of methanol and water when the system was operated for a certain period at a rated system output of 130 W, stack voltage and current, power consumption of BOP such as pumps and fans, and temperatures at the six locations shown in Fig. 1, i.e., stack temperature, stack-anode inlet and outlet temperatures, stack-cathode inlet and outlet temperatures, and outlet temperature of the condenser. The evaluation items were the efficiencies of cell, fuel, stack, and system. The efficiency was calculated in the HHV.

The cell voltage efficiency ηcell is obtained by dividing the voltage at the time of power generation by the theoretical electromotive force, which is the Gibbs energy change divided by the number of reacting electrons and the Faraday constant, following the Nernst equation. This is expressed as follows:

\[ η_{cell} = \frac{V(T) - ΔG^o}{-6F} \times 100 \]  \hspace{1cm} (41)

The fuel efficiency ηfuel is defined as the value obtained by dividing the amount of methanol consumed in the power-generation reaction by the total amount of methanol consumed during system operation.

Under the assumption that the methanol consumed by the system operation, excluding the methanol consumed by power generation, is moved to the cathode side by MCO, ηfuel is calculated as follows:

\[ η_{fuel} = \frac{\dot{m}_{an,cons,M}}{\dot{m}_{an,cons,M} + \dot{m}_{an,cons,M}^{\text{cross}}} \times 100 \]  \hspace{1cm} (42)

Further, the stack energy efficiency ηSTK is obtained by multiplying cell efficiency by fuel efficiency as follows:

\[ η_{STK} = η_{cell} \times η_{fuel} \]  \hspace{1cm} (43)

Finally, the system efficiency ηsys is defined as the value obtained by subtracting the power consumption of the auxiliary equipment from the stack output power and dividing the value obtained by the total methanol energy consumed during system operation as follows:

\[ η_{sys} = \frac{P_{STK} - P_{BOP}}{-28 V \times (\dot{m}_{an,cons,M} + \dot{m}_{an,cons,M}^{\text{cross}})} \times 100 \]  \hspace{1cm} (44)

where \( P_{STK} \) and \( P_{BOP} \) are the stack output power (W), BOP power (W), respectively.

3. Results and Discussion

3.1 Polarization characteristics of DMFC based on experimental results

Figure 5a shows the current density–voltage characteristics of a single cell at various temperatures with a methanol concentration of 3 wt%. The cell voltage exhibits a monotonous increase with an increase in the cell temperature, probably because of the reduction in the proton-conductive resistance and charge-transfer resistances owing to the methanol oxidation and oxygen reduction, respectively. In contrast, the cell voltage experienced only a slight enhancement when the temperature was increased to 90°C. According to Fig. 5b, the slope of the Arhenius plot became smaller above 80°C (below 2.83 K⁻¹), which might be affected by the methanol crossover enhanced by the cell temperature rise.

Figure 6 shows the experimental results of the polarization characteristic of 51 cell DMFC stack. The peak power output of the stack reached 298 W at 0.31 A cm⁻². The net power output of the DMFC system after consuming the BOP power was maintained at 130 W in steady-state operation with a constant load at room temperature. As a result of measuring the voltage of each cell in the stack, the variation of each cell voltage was within ±0.23% of the average cell voltage. Because the stack was self-heated in the system, the stack temperature was maintained in the temperature range of 55 to 65°C by controlling the BOP. Simultaneously, the BOP power consumption was in the range of 34–20 W. The typical operating voltage in this case was approximately 24–28 V.
by the analysis resulted in an accuracy of $-3.7\%$ of the heating amount by actual measurement. This insufficient cooling is believed to be a result of the settings of certain preconditions; however, it is presumed that the primary cause is that heat transfer in the mixing tank was not considered.

### 3.3 Dependence of electrical efficiency on stack temperature

The heat and mass balances at stack temperatures from 50°C to 80°C were analyzed, and the effect of stack temperature on electrical efficiency was investigated by constraining the conditions of the BOP parameters on the anode side and focusing on the operating conditions on the cathode side. Specifically, the stack temperature with the air flow rate on the cathode side was controlled. The parameters used in the analysis are listed in Table 5. Table 6 lists the calculation results for the mass balance of the stack, electrical efficiency, and required exchanged heat of the condenser.

Figure 8 shows the temperature dependence of the fuel, cell voltage, stack energy, and system efficiencies. The system efficiency attained a maximum of 21.8% HHV at a stack temperature of 60°C and thereafter decreased with increasing stack temperature. In contrast, the stack energy efficiency decreased monotonically with increasing stack temperature, indicating that the system efficiency peaked because of the BOP loss caused by the increase in the cathode air flow rate.

### Table 3. Operation data of DMFC system

| No. | Parameter                  | Unit | Value  |
|-----|----------------------------|------|--------|
| 1   | Stack voltage              | V    | 24.5   |
| 2   | Stack current              | A    | 7.0    |
| 3   | Electrode area             | cm²  | 75.26  |
| 4   | Number of cells            |      | 51     |
| 5   | Stack temperature          | °C   | 65.0   |
| 6   | Anode inlet temperature    | °C   | 56.0   |
| 7   | Anode outlet temperature   | °C   | 65.9   |
| 8   | Cathode inlet temperature  | °C   | 25.7   |
| 9   | Cathode outlet temperature | °C   | 65.9   |
| 10  | Environmental temperature  | °C   | 25.7   |
| 11  | Methanol concentration     | wt%  | 2.3    |
| 12  | Fuel-cartridge consumption | g min⁻¹ | 2.67 |
| 13  | Water-cartridge consumption| g min⁻¹ | 3.90 |

### Table 4. Results of heat balance analysis.

| No. | Parameter                          | Unit                  | Value  |
|-----|------------------------------------|-----------------------|--------|
| 1   | Total heat value                    | W                     | 486    |
| 2   | Electric power                      | W                     | 171    |
| 3   | Heat associated with power generation | W                | 260    |
| 4   | Heat associated with MCO            | W                     | 226    |
| 5   | Heat of vaporization of MCO methanol | W                 | 1.1    |
| 6   | Heat of vaporization of cathode-generated water | W | 303    |
| 7   | Stack heat dissipation              | W                     | 17     |
| 8   | Required amount of cooling heat     | W                     | 164    |
| 9   | Anode-outlet sensible heat          | kJ kg⁻¹               | 273    |
| 10  | Anode inlet sensible heat           | kJ kg⁻¹               | 232    |
| 11  | Anode-outlet gas sensible heat      | kJ kg⁻¹               | 64     |
| 12  | Anode-outlet liquid flow rate       | g s⁻¹                 | 3.854  |
| 13  | Anode-inlet liquid flow rate        | g s⁻¹                 | 4.141  |
| 14  | Anode-outlet gas flow rate          | g s⁻¹                 | 0.031  |
| 15  | Anode heat of vaporization         | W                     | 10     |
| 16  | Anode cooling amount               | W                     | 100    |
| 17  | Gas sensible heat at cathode outlet | kJ kg⁻¹               | 76.8   |
| 18  | Gas sensible heat at cathode inlet  | kJ kg⁻¹               | 26.1   |
| 19  | Liquid sensible heat at cathode outlet | kJ kg⁻¹         | 275.8  |
| 20  | Gas flow rate at cathode outlet     | g s⁻¹                 | 0.8    |
| 21  | Gas flow rate at cathode inlet      | g s⁻¹                 | 0.7    |
| 22  | Liquid flow rate at cathode outlet  | g s⁻¹                 | 1.5    |
| 23  | Cathode cooling amount             | W                     | 48     |
| 24  | Anode/cathode total cooling amount | W                     | 148    |
| 25  | Balance                             | %                     | −3.4   |
| 26  | System efficiency                  | % HHV                 | 21.5   |
| 27  | System efficiency (actual measurement) | % HHV               | 23.9   |

Figure 6. Stack voltage (●) and power (■) vs. current density of 51 cell DMFC stack obtained experimentally at 25°C.
Further, the cell voltage efficiency increased with increasing temperature by improving the catalyst activity. The improvement of the anode activity loss, which is among the most important issues in DMFCs, is considered to be the main contributor to the improvement of the cell voltage efficiency, although the decrease in the cathode potential caused by the mixed potential by MCO may also have an influence on the cell voltage.

Furthermore, the fuel efficiency decreased monotonically with increasing stack temperature, and the stack energy efficiency exhibited a similar trend. This indicates that the decrease in the fuel efficiency by MCO is more dominant than the improvement in the cell voltage efficiency with respect to the decrease in the stack energy efficiency.

The results of the heat balance analysis are presented in Table 7, which reveal that the following three phenomena, shown in Fig. 9, change relatively significantly as the stack temperature changes. The results suggest that both MCO and WCO may influence system efficiency.

- Heat associated with power generation
- Heat associated with MCO
- Heat of evaporation of water produced at cathode

WCO increases with increasing temperature, and an increase in the WCO increases the amount of cooling of the stack owing to the latent heat of vaporization. According to the proposed heat and mass balance analysis model, when the stack temperature is 80 °C, the amount of heat generated by MCO increases by 343 W. In contrast, the latent heat of WCO is expected to cool the stack by 426 W; that is, the amount of cooling by the auxiliary equipment can be reduced in total. Therefore, the auxiliary equipment loss due to reduced air flow is expected to be reduced.

The amount of anode-side cooling at 80 °C has a negative sign (Table 7 No. 16), suggesting that it does not contribute to cooling.

**Table 5.** Numerical parameters used in the analysis.

| No. | Parameter                      | Unit          | Value          |
|-----|--------------------------------|---------------|----------------|
|     |                                |               | 50 °C | 55 °C | 60 °C | 65 °C | 70 °C | 80 °C |
| 1   | Stack voltage                  | V             | 22.3  | 24.0  | 25.4  | 26.5  | 26.7  | 27.9  | Measured data |
| 2   | Current density                | mA cm⁻²       | 106   | 91    | 82    | 76    | 74    | 68    | Measured data |
| 3   | Electrode area                 | cm²           | 75.26 | 75.26 | 75.26 | 75.26 | 75.26 | 75.26 | Precondition |
| 4   | Number of cells                | —             | 51    | 51    | 51    | 51    | 51    | 51    | Precondition |
| 5   | Stack temperature              | °C            | 50    | 55    | 60    | 65    | 70    | 80    | Precondition |
| 6   | Anode inlet temperature        | °C            | 45    | 50    | 54    | 58    | 64    | 70    | Precondition |
| 7   | Anode outlet temperature       | °C            | 50    | 55    | 60    | 65    | 70    | 80    | Precondition |
| 8   | Cathode inlet temperature      | °C            | 25    | 25    | 25    | 25    | 25    | 25    | Precondition |
| 9   | Cathode outlet temperature     | °C            | 50    | 55    | 60    | 65    | 70    | 80    | Precondition |
| 10  | Environmental temperature      | °C            | 25    | 25    | 25    | 25    | 25    | 25    | 25 °C 40 % RH |
| 11  | Methanol concentration         | wt%           | 3     | 3     | 3     | 3     | 3     | 3     | Precondition |
| 12  | Air flow rate                  | L min⁻¹       | 89.0  | 62.0  | 45.0  | 35.0  | 31.0  | 19.0  |               |
| 13  | Fuel flow rate                 | L min⁻¹       | 0.25  | 0.25  | 0.25  | 0.25  | 0.25  | 0.25  | Precondition |
| 14  | BOP power                      | W             | 48.2  | 34.7  | 26.2  | 21.2  | 19.2  | 13.2  | Measured data |
| 15  | System output                  | W             | 130.0 | 130.1 | 130.1 | 130.1 | 130.0 | 130.1 |               |

**Figure 7.** Results of heat-balance analysis at stack temperature of (a) 65 °C (Case 1) and (b) 55 °C (Case 2).
and this can attribute to the increase in WCO. Therefore, it is considered that the water flow rate on the anode outlet side decreases, and the amount of heat that can be extracted decreases. However, the sensible heat of the liquid on the cathode side is increased by the amount of decrease, and thus the overall heat balance is correct.

Although this phenomenon causes no thermal effects, it is considered undesirable when considering the power generation environment because the heat extracted by sensible cooling is transferred from the anode side to the cathode side. The reason for this is that water impedes the supply of oxygen to the cathode. A serious problem concerning a DMFC is the flooding on the cathode side. This phenomenon is the primary reason for the difficulty faced in increasing the oxidant utilization rate of DMFCs compared to other fuel cells. Therefore, the ideal amount of WCO is the amount that enhances the effect of latent heat cooling but does not produce condensed water that causes flooding and plugging. Thus, ideally, the WCO should be controlled to an amount that can secure the latent heat required for cooling within the range wherein the relative humidity on the cathode side does not exceed 100%.

Therefore, the future development of new electrolyte membrane materials that can suppress MCO and WCO at high temperatures is

![Figure 8](image_url)
expected to improve system efficiency by increasing the stack operating temperature. MCO and WCO can also be suppressed by increasing the thickness of the electrolyte membrane. If MCO and WCO could be described as a function of membrane thickness, this model will give the optimize thickness of the membrane.

Regarding the analysis results for the condenser listed in Table 6, initially, the increase in saturated water vapor pressure due to high temperature can reduce \( T \) required for condensation and increase \( T \) between the environmental temperature and the condenser. Consequently, the amount of heat required for exchange is expected to be reduced. However, according to the analysis results, the amount of recovered water increased due to the increase in the amount of WCO, thus, the required amount of heat exchanged increased.

Although the results will be reflected in the future development of condensers, this analysis revealed that the reduction in WCO volume (i.e., reduction of required water-recovery volume), which leads to a reduction in the required exchange area and cooling-air volume, is an important parameter for downsizing condensers and increasing their efficiency. Because WCO is considered to be affected not only by the material properties but also by the supply-air flow rate, as a future task the dependence of WCO amount on oxidant utilization rate needs to be understood such that the optimum oxidant-utilization-rate range considering the system efficiency can be determined.

## 4. Conclusions

In this study, an analysis model for the heat and mass balances of a DMFC system was proposed, considering the experimental data of the DMFC and the heat and mass transfer in the system. The model can predict the mass and heat transfer, heat balance, and electrical

![Figure 9. Temperature dependence of heat of vaporization of cathode-generated water (●), heat associated with power generation (▲), and heat associated with MCO (●) and WCO (×).](image-url)
efficiency of the DMFC. Based on results of using this model to investigate the effect of stack temperature on the electrical efficiency of a DMFC system, the following conclusions were drawn.

- According to the system efficiency calculation results from the measured data of the system, the calculated efficiencies at stack temperatures of 55 °C and 65 °C were 22.7% HHV (measured value: 25.2% HHV) and 21.5% HHV (measured value: 23.9% HHV), respectively. These results show that the prediction can be made correctly with an accuracy of approximately 2.5%.
- The effect of stack temperature on the electrical efficiency of the DMFC system was investigated, and the results showed that (i) the optimum stack temperature at a system power of 130 W is 60 °C and (ii) the system efficiency at that temperature is 21.8% HHV.
- The results of this analysis revealed that the required exchange heat of the condenser increased as the WCO amount increased with increasing temperature.

Although DMFCs are less efficient than other fuel cells, the requirements of users for portable power sources are (a) silence, (b) clean (indoor or in-vehicle use), (c) continuous use, and (d) off-grid and emergency use. Useful applications of DMFC systems to meet the above needs include power sources for shooting on location in the broadcasting field, power sources for portable equipment such as hospital rounds in the medical field, auxiliary power sources for emergency vehicle equipment in the public sector, and emergency power sources in disaster situations. In the above applications, engine generators and/or rechargeable batteries are currently used, however, they do not fully satisfy the above four needs of users, hence there are high expectations for DMFC systems as a portable power source.

The presented model is a useful tool for understanding DMFCs in operation and for optimizing fuel cell designs. Further, the model is sufficiently light in terms of computation to be calculated with common spreadsheet software, and can be implemented in a system and field tested with the above applications to identify issues and obtain feedback using measurable data from the system to help improve the efficiency of DMFC systems. The model is expected to contribute to the widespread use of DMFC systems in the future.

**Nomenclature**

**Latin symbols**

| Symbol | Description |
|--------|-------------|
| $A$    | electrode area (cm²) |
| $c_M$  | methanol concentration (wt%) |
| $C_p$  | specific heat (kJ kg⁻¹ K⁻¹) |
| $F$    | Faraday constant (96485 A s mol⁻¹) |
| $\Delta G(T)$ | change of Gibbs energy at temperature $T$ (J mol⁻¹) |
| $H$    | enthalpy (J mol⁻¹) |
| $I$    | current density (A cm⁻²) |
| $M_{CO_2}$ | molar mass of CO₂ (0.044 kg mol⁻¹) |
| $M_{H_2O}$ | molar mass of water (0.018 kg mol⁻¹) |
| $M_M$  | molar mass of methanol (0.032 kg mol⁻¹) |
| $M_O_2$ | molar mass of oxygen (0.032 kg mol⁻¹) |
| $m_j$  | mass flow rate of species $j$ (g s⁻¹) |
| $N_j$  | number of cells used in a stack |
| $P_{STK}$ | fuel-cell-stack power output (W) |
| $P_{BOP}$ | power demand of auxiliary components (W) |
| $Q$    | heat generation (W) |
| $q_j$  | evaporation heat of species $j$ (kJ kg⁻¹) |
| $S$    | entropy (J mol⁻¹ K⁻¹) |
| $S_a$  | surface area of fuel-cell stack (m²) |

**Greek symbols**

| Symbol | Description |
|--------|-------------|
| $\alpha$ | reaction rate of methanol transferred to the cathode by methanol cross-over (%) |
| $\beta$ | constant (—) |

**Superscripts and Subscripts**

| Symbol | Description |
|--------|-------------|
| an     | anode |
| BOP    | balance of plant |
| ca     | cathode |
| cell   | fuel cell |
| cond   | condenser |
| cons   | consumption due to electrochemical reactions |
| fuel   | fuel |
| gas    | gas phase |
| gen    | production due to electrochemical reactions |
| HHV    | higher heating value |
| in     | entering |
| liq    | liquid phase |
| out    | exiting |
| RH     | relative humidity |
| STK    | fuel-cell stack |
| lat    | latent heat |

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**Conflict of Interest**

The authors declare no conflict of interest in the manuscript.

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