Exergy analysis of polymer electrolyte fuel cell systems using methanol

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Abstract

An exergy (available energy) analysis has been conducted on a typical polymer electrolyte fuel cell (PEFC) system using methanol. The material balance and enthalpy balance were calculated for the PEFC system using methanol steam reforming, and the exergy flow was obtained. Based on these results, the exergy loss in each unit was obtained, and the difference between the enthalpy and exergy was discussed. The exergy loss in this system was calculated to be 193 kJ/mol MeOH for the steam reforming process of methanol. Although the enthalpy efficiency approached unity as the recovery rate of the waste heat from the cell approached unity, the exergy efficiency remained around 0.45 since the cell's operating temperature of 80 °C is low. It was also found that the cell voltage should exceed 0.82 V in order to obtain the exergy efficiency of 0.5 or higher. A direct methanol fuel cell (DMFC) was analyzed using the exergy and compared with the methanol reforming PEFC. In order to obtain the exergy efficiency higher than that of PEFC with steam reforming, the cell voltage of the DMFC should be 0.50 V or larger at the current density of 600 mA/cm^2.
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1. Introduction

The conversion efficiency is the most important factor for an energy system, especially using fossil fuels. The CO_2 emission is directly related to the conversion efficiency. In order to analyze the entire system, each unit of the system should be carefully analyzed and the quality of energy should be considered. Generally, the efficiency of the energy conversion is considered through the enthalpy balance, which is based on the first law of thermodynamics. It is possible that the enthalpy efficiency of a conversion system approaches unity by the promotion of the heat recovery, even if the system is irreversible, since the enthalpy does not contain the concept of irreversibility. The entropy of the total system increases due to the irreversibility, which means the diversion of the energy. The quality of energy decreases through the conversion system. The exergy concept should be used for the evaluation of the efficiency considering the irreversibility. The exergy is often called the available en-

ergy. The exergy analysis is better than an enthalpy balance because exergy can deal with the quality of energy and evaluate different forms of energy like chemical, thermal and electrical energy by a unified measure. In addition, the degree of irreversibility in each element of the system could be quantitatively discussed. Through the exergy analysis, we can easily find the unit that has a large exergy loss and provide guidelines for improving the conversion system.

In the field of chemical engineering and mechanical engineering, the exergy analysis is widely carried out [1–4]. For the fuel cell, Rosen and coworkers have compared various types of fuel cells such as the phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), polymer electrolyte fuel cell (PEFC) and solid oxide fuel cell (SOFC) [5,6]. They emphasized that the exergy analysis should be used when examining the co-generation potential of the fuel cell systems. However, they estimated the exergy efficiency based only on exergy of the fuel, cell voltage and waste heat, and the irreversibility of each element was not mentioned in detail. The effect of the difference in fuel feed system on the exergy efficiency has been compared to a SOFC [7]. Van den Oosterkamp et al. have shown that the exergy was useful

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for the analysis of the fuel cell system [8]. However, very few papers have reported the irreversibility of the system element in detail for a PEFC. The PEFC is under development for use in electric vehicles and co-generation systems, because of its high power density and low temperature operation. The optimization of its efficiency and process operation is a major issue in system development.

In this study, the methanol reforming PEFC system was treated, and the material balance and enthalpy balance through the system were first calculated. The exergy loss in each unit was then quantified, and the difference between the enthalpy and exergy was discussed. The essential irreversibility of the methanol reforming PEFC was considered throughout the analysis. The effect of exhaust heat recovery from the cell and cell voltage on the enthalpy or exergy efficiency was also examined. These results were compared with a direct methanol fuel cell (DMFC) where methanol was directly used as the fuel.

2. Theory

The second law of thermodynamics indicates the restriction of the transformation of energy from one form into another. The exergy is defined as the maximum amount of work that can be extracted from the substance as it undergoes a reversible process from a given state to the environmental state. The general equation of the exergy ε is expressed as following equation:

$$\varepsilon = (H - H_0) - T_0(S - S_0) \tag{1}$$

where H and S respectively denote enthalpy and entropy; T denotes the absolute temperature; the subscript 0 denotes properties evaluated at the environment reference state. According to Eq. (1), the exergy destructs, as the entropy increases in the irreversible process. Thus, exergy balance can be written as

$$\varepsilon_{\mathrm{in}} = \varepsilon_{\mathrm{out}} + \varepsilon_{\mathrm{diss.}} + \varepsilon_{\mathrm{dest.}} \tag{2}$$

where $\varepsilon_{\mathrm{in}}$, $\varepsilon_{\mathrm{out}}$, $\varepsilon_{\mathrm{diss.}}$ and $\varepsilon_{\mathrm{dest.}}$ respectively denote exergy input, exergy output, exergy dissipation and exergy destruction. The exergy loss in the process is shown in Fig. 1. Total exergy loss $\varepsilon_{\mathrm{loss}}$ the process can be calculated as a difference between exergy input and output, and can be written as

$$\varepsilon_{\mathrm{loss}} = \varepsilon_{\mathrm{in}} - \varepsilon_{\mathrm{out}} = \varepsilon_{\mathrm{diss.}} + \varepsilon_{\mathrm{dest.}} \tag{3}$$

The first term on the right hand side $\varepsilon_{\mathrm{diss.}}$ represents the exergy dissipation which is unused (exergy loss I). On the other hand, the second term on the right hand side $\varepsilon_{\mathrm{dest.}}$ represents the exergy destruction due to the irreversibility of the system (exergy loss II). The exergy destruction due to the irreversibility generates when chemical reaction, heat transfer, pressure drop and mixing proceed in the process. Table 1 shows the fundamental exergy equations.

Exergy analysis requires that the environment is defined. Here, temperature and pressure of the environment were set
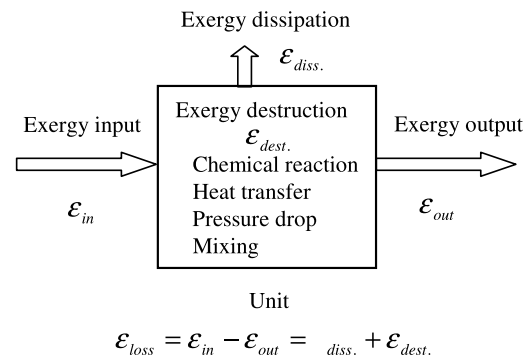

Fig. 1. Exergy balance in a unit.

Table 1
Fundamental exergy equations

Form of exergy	Equation
Chemical	$\varepsilon_{\mathrm{C}} = \sum n_i \varepsilon_i^0$
Thermal	$\varepsilon_{\mathrm{T}} = \left(\sum n_i C_{p,i}\right)\left\{T - T_0 - T_0 \ln\left(\dfrac{T}{T_0}\right)\right\}$
Mechanical	$\varepsilon_{\mathrm{Me}} = \left(\sum n_i\right) R T_0 \ln\left\{\sum\left(\dfrac{P_i}{P_0}\right)\right\}$
Mixing	$\varepsilon_{\mathrm{Mi}} = R T_0 \sum\left[n_i \ln\left\{\dfrac{n_i}{\sum n_i}\right\}\right]$

$\varepsilon = \varepsilon_{\mathrm{C}} + \varepsilon_{\mathrm{T}} + \varepsilon_{\mathrm{Me}} + \varepsilon_{\mathrm{Mi}}$.

Table 2
Environmental conditions for exergy analysis

Condensed phase	Gas phase	
	Substances	Mole fraction
$H_2O(l)$ at T_0, P_0	N_2	0.7560
	O_2	0.2034
	H_2O	0.0312
	CO_2	0.0003
	Ar	0.0091

$T_0 = 25\,^\circ\mathrm{C}$, $P_0 = 1\,\mathrm{atm}$.

equal to the reference temperature and pressure (298.15 K, 1 atm). The environmental conditions are shown in Table 2.

Table 3 shows the value of the standard chemical exergy of the substances which are related to the fuel cell system. The selection of the standard substance was based on Japanese

Table 3
Standard chemical exergy of substances

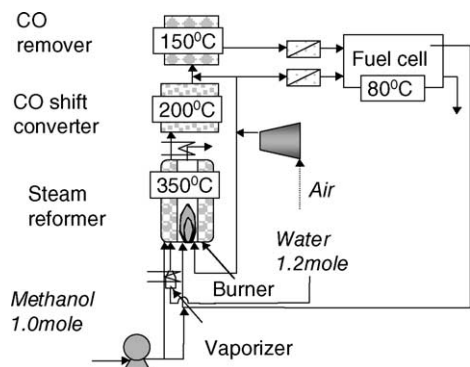| Substances	Reference substance	ε^0 (kJ/mol)
$H_2(g)$	$H_2O(l)$	235.39
$CO(g)$	$CO_2(g)$	275.55
$CO_2(g)$	Air	20.11
$CH_3OH(g)$	$H_2(g)$, $CO(g)$	721.80
$N_2(g)$	Air	0.71
$O_2(g)$	Air	3.94
$H_2O(g)$	$H_2O(l)$	8.58
$CH_3OH(l)$	$CH_3OH(g)$	717.23
$H_2O(l)$	$H_2O(1)$	0

$T_0 = 25\,^\circ\mathrm{C}$, $P_0 = 1\,\mathrm{atm}$.

Fig. 2. Modeling of methanol reforming PEFC.

Industrial Standard (JIS). For the calculation of enthalpy balance, the final state, $CO_2(g)$ and $H_2O(l)$ at the reference temperature and pressure, is defined as a reference state, and the enthalpy difference, referred to the reference state, was utilized. Therefore, the enthalpy value of initial state, $CH_3OH(l)$ and $H_2O(l)$, could be calculated to be 728 kJ.

3. Modeling of methanol reforming PEFC

The methanol reforming PEFC is composed of a series of the following units as shown in Fig. 2:

vaporizer → steam reformer → CO shift converter

→ CO remover → fuel cell → burner

Liquid methanol and water are vaporized at 100 °C in vaporizer. Methanol gas converts to hydrogen at the steam reformer by steam reforming reaction. Simultaneously, water gas shift reaction occurs, and carbon monoxide is produced. In order to remove carbon monoxide less than about 10 ppm, CO shift converter and CO remover process were added.

Fuel gas should be heated at the reformer where the steam reforming reaction takes place around 350 °C. Since the steam reforming reaction is endothermic, adequate heat should be supplied to maintain the reaction temperature. The required heat in this model for warming the fuel and gases, and the endothermic process heat of the steam reformer was

supplied by controlling the rate of hydrogen utilization in the cell. Generally, the fuel (hydrogen) was not thoroughly consumed in the cell, and the remaining hydrogen was burnt in the burner, and the process heat was generated. The S/C ratio of the fuel was assumed to be 1.2. The oxygen necessary for the reaction in the CO remover and as the oxidant in the cell reactor was taken from air. A 5% excess quantity of oxygen was introduced in order to remove CO by combustion. The excess oxygen caused the burning of hydrogen. The waste heat in the cell was not returned in the system in this study for simplification. In this paper, in order to investigate the influence of the improvement of the cell performance, the cell voltage U (V) was a variable. The other modeling conditions of each unit are shown in Table 4.

A 71.4 kJ/mol MeOH enthalpy is necessary for the endothermic reaction of steam reforming, and 158.9 kJ is necessary for the warming of the fuel and gases. (The sum of necessary heat is 230.3 kJ/mol MeOH.) Within the combustion heat of 166.1 kJ, which is generated in the burner, 71.4 kJ was supplied for the endothermic reaction of steam reforming, and the rest 97.7 kJ was supplied to the vaporizer. A 61.2 kJ (=158.9–97.7 kJ) enthalpy necessary for the warming was supplied by the heat exchange with exhaust gases in the burner.

4. Results and discussion

4.1. Material flow, enthalpy flow and exergy flow

Using the above-mentioned model, the material balance and enthalpy balance were calculated for 1 mol of methanol, and the reaction values in each unit were obtained. The material balance and enthalpy balance depended on the heat quantity, and they were independent of the cell voltage. The amounts of the substances in the system are shown in Table 5. In this table, the numbers on the upper line correspond to those in Figs. 3 and 4.

Figs. 3 and 4 showed the flow of enthalpy and exergy calculated from the material flow. The exergy loss in a unit is shown in the parenthesis of each unit in Fig. 4. Here, the heat release due to the temperature drop from one unit to the next

Table 4
Modeling condition of each unit in methanol reforming PEFC

Unit	Temperature (°C)	Reaction	Condition
Vaporization	100	$CH_3OH(l) \rightarrow CH_3OH(g)$, $H_2O(l) \rightarrow H_2O(g)$	
Steam reformer	350	$CH_3OH(g) + H_2O(g) = 3H_2(g) + CO_2(g)$, $H_2(g) + CO_2(g) = H_2O(g) + CO(g)$	The equilibrium composition was achieved
CO shift converter	200	$H_2O(g) + CO(g) = H_2(g) + CO_2(g)$	The equilibrium composition was achieved
CO remover	150	$CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$	CO was burnt with the oxygen, until it became 10 ppm at the CO concentration
Fuel cell	80	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $(1/2)O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$	Cell voltage: U (V) Oxygen utilization rate was assumed to be 40%
Burner	350	$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(g)$	Heat exchange efficiency was assumed to be 80%

Table 5
Mass balance (mol) of methanol reforming PEFC system

	1	2	3	4	5	6	7	8	9	10	11
Anode											
$CH_3OH(l)$	1.000	–	–	–	–	–	–	–	–	–	–
$CH_3OH(g)$	–	1.000	–	–	–	–	–	–	–	–	–
$H_2O(l)$	1.200	–	–	–	–	–	–	–	–	–	0.819
$H_2O(g)$	–	1.200	0.435	0.249	–	0.251	–	–	0.251	–	0.110
$H_2(g)$	–	–	2.765	2.951	–	2.949	–	–	0.678	–	–
$CO(g)$	–	–	0.235	0.049	–	5×10^{-5}	–	–	5×10^{-5}	–	–
$CO_2(g)$	–	–	0.765	0.951	–	1.000	–	–	1.000	–	1.000
$O_2(g)$	–	–	–	–	0.026	–	–	–	–	0.356	0.017
$N_2(g)$	–	–	–	–	0.102	0.102	–	–	0.102	1.424	1.526
Cathode											
$O_2(g)$	–	–	–	–	–	–	2.839	1.703	–	–	–
$N_2(g)$	–	–	–	–	–	–	11.36	11.36	–	–	–
$H_2O(l)$	–	–	–	–	–	–	–	2.271	–	–	–
Temperature (°C)	25	350	200	150	150	80	80	80	80	350	100

Fig. 3. Enthalpy flow in methanol reforming PEFC system (per 1 mol of methanol).

is shown as the heat release from the unit in the front. For example, the heat release of 20 kJ, which was accompanied by the temperature drop from the steam reformer at 350 °C to the CO shift converter at 200 °C was included for the steam reformer unit. This heat release was not recovered in the system based on a realistic point of view.

The exergy loss in each unit except for the cell is shown in Fig. 5. The total exergy loss in a unit except for the cell in this methanol reforming PEFC system was 193 kJ/mol MeOH. There are two kinds of exergy losses. One is a loss (exergy loss I) based on the un-recovered heat. Though this

Fig. 4. Exergy flow in methanol reforming PEFC system (per 1 mol of methanol).

Fig. 5. Exergy loss at each unit.

Table 6
Exergy loss and enthalpy change due to chemical reaction

Unit (temperature) chemical reaction	Extent of reaction (mol)	Enthalpy change (kJ)	Exergy loss (kJ)	Heat recovery (in terms of exergy/kJ)
Steam reformer (623 K)				
$CH_3OH(g) + H_2O(g) = 3H_2(g) + CO_2(g)$	1.000	62.3	37.04	–
$H_2(g) + CO_2(g) = CO(g) + H_2O(g)$	0.235	9.06	10.03	–
CO shift converter (473 K)				
$CO(g) + H_2O(g) = H_2(g) + CO_2(g)$	0.186	−7.44	5.26	×
CO remover (423 K)				
$CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$	0.049	−13.78	12.62	×
$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(g)$	0.002	−0.59	0.55	×
Fuel cell reactor (353 K, U (V))				
$H_2(g) + 2e^- \rightarrow 2H^+$	2.271	−645.73	538.7–438.2U	See Section 3
$(1/2)O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l)$				
Burner (623 K)				
$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(g)$	0.678	−166.05	155.8	86.6

is theoretically retrievable, it becomes a loss in this study, because the waste heat is not recovered in this model. The sum of exergy loss I is 36 kJ/mol MeOH. The other is the essential loss (exergy loss II) based on the irreversibility. Unlike exergy I, this cannot be fundamentally recovered. The sum of exergy loss II is 156 kJ/mol MeOH.

The enthalpy change and exergy loss with the chemical reaction in each unit are shown in Table 6. The exergy loss of the hydrogen burning reaction in the burner is as large as 155.8 kJ. However, the heat from the burner was supplied to warm the fuel and gases, that is to say, the exergy was recovered to the system. The value of recovered exergy is 86.6 kJ. Therefore, the net exergy loss of the hydrogen burning is 69.2 kJ. The enthalpy and exergy efficiencies were defined as the ratio of the input and output enthalpy and exergy, respectively. The electrical energy generated in the cell was expressed as follows:

$$\text{electrical energy} = nF\xi U \tag{4}$$

where n is the electron number of the cell reaction, F is the Faraday constant and ξ is the extent of reaction in the cell. Since the extent of reaction in the cell is 2.27 mol, the electric energy generated in the cell is 438U kJ. Therefore, the relationship between the enthalpy, exergy efficiencies and cell voltage of the present model are given by the following equations:

$$\text{enthalpy efficiency} = \frac{1}{728} \times 438U = 0.602U \text{ (V)} \tag{5}$$

$$\text{exergy efficiency} = \frac{1}{722} \times 438U = 0.607U \text{ (V)} \tag{6}$$

The following points are noted from Figs. 3–5 and Table 6.

1. The hydrogen utilization of the cell in this PEFC system was 75.0%. The remaining hydrogen (25%) was mainly used for the supplying heat for the steam reforming process.
2. The enthalpy and exergy efficiencies are functions of the cell voltage U, and they were 60.2U% and 60.7U%, respectively, when the waste heat in the cell was not recovered.
3. The enthalpy for the supply of heat for fuel and warming of the gas, and the endothermic reactions in the steam reformer was 230 kJ. In particular, the enthalpy supplied to the vaporizer was as high as 121 kJ, and it was about 50% overall (230 kJ). In comparison with the other warming process, it was shown that significant enthalpies are necessary for the evaporation of the liquid methanol and water.
4. The total exergy loss in a unit except for the cell in this methanol reforming PEFC system was 193 kJ/mol MeOH. That is to say, the exergy loss of 193 kJ was inevitable for this system. This corresponded to 27% of the 722 kJ exergy of 1 mol of methanol.
5. The enthalpy in the steam reformer increases 71 kJ (62 + 9 kJ), because the reactions in the steam reformer were endothermic. However, the exergy in the steam reformer decreased 47 kJ (37 + 10 kJ), since the endothermic reaction in the steam reformer was irreversible.
6. In a unit except for the cell, the maximum exergy loss occurred at the burner. The exergy loss of 86 kJ corresponded to 44% of the total exergy loss (193 kJ) except for the cell.
7. In this model, the total of the un-recovered exergy except for the cell was 36 kJ. This corresponded to 19% of all the exergy losses except for the cell.

4.2. Effect of the exhaust heat recovery from the cell on the system efficiency

According to the enthalpy balance method, the increase in the heat recovery is effective in order to increase the system efficiency. However, the increase in the heat recovery does not remarkably improve the exergy efficiency, since the temperature of the heat should be accounted for in the exergy analysis. The effect on the enthalpy and exergy efficiency of
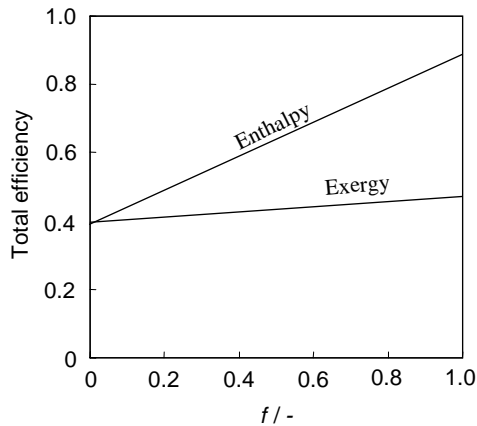
Fig. 6. The relation between total efficiency and heat utilization of fuel cell.

Fig. 7. Dependence of total exergy efficiency and exergy loss of the cell on cell voltage.

the exhaust heat recovery from the cell was compared when the cell voltage was assumed to be 0.65 V. When the cell voltage is 0.65 V, the electrical energy (exergy) generated in the cell becomes 285 kJ, and the enthalpy of the waste heat is 361 kJ. This corresponds to a 56 kJ exergy when the cell temperature is 80 °C. In Fig. 6, the effect of the recovery rate, f, of the waste heat from the cell on each efficiency is shown. The enthalpy efficiency approaches unity as the recovery rate of waste heat approaches unity. The promotion of the exhaust heat recovery is proved to be effective in increasing the enthalpy efficiency. However, the exergy efficiency remains around 0.45, even if all the waste heat is recovered ($f = 1$). In other words, it is proved that the increase in the exergy efficiency is very small, even if the recovery of waste heat in the cell is promoted. This is because the cell's operating temperature of 80 °C is low. Though the low temperature operation is an advantage of the PEFC for the easy operation, it is disadvantageous to increase the exergy by the recovery of exhaust heat from the cell.

For the enthalpy efficiency, only the quantity of heat is important, and the quality is not considered. For the exergy efficiency, the quality of heat (temperature of heat) is also important. Low temperature heat has a small activity to produce work. When the heat recovery is promoted to improve the efficiency, the efficiency of the system should be discussed using the exergy, which contains the concept of availability.

4.3. Effect of the cell voltage on the exergy efficiency

The cell voltage of present PEFC is about 0.65 V at 600 mA/cm^2 [9]. The exergy efficiency becomes 39.8% when cell voltage is 0.65 V. Since the operating temperature of the cell is low, in the case of the PEFC, the recovery of the waste heat from the cell does not bring about a remarkable increase in the exergy efficiency, as previously described. Therefore, it is necessary to increase the electrical energy generated in the cell in order to raise the exergy efficiency.
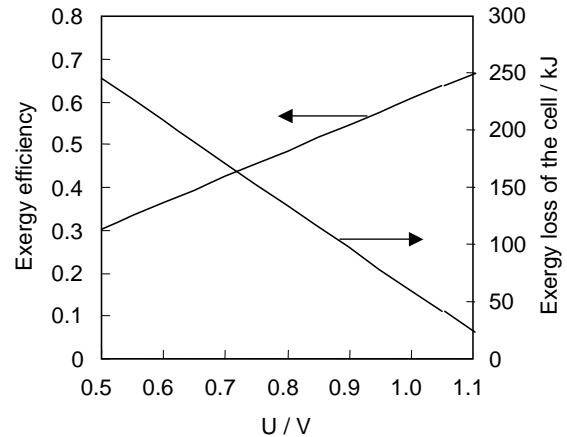
When the hydrogen utilization and/or cell voltage increase at the same current density, the electrical energy from the cell may increase. However, it is difficult to increase the hydrogen utilization, because a supply of heat is necessary for the methanol reforming process. Therefore, increasing the cell voltage is the only way to raise the exergy efficiency. The effect of the cell voltage on the exergy efficiency is shown in Fig. 7. In the same figure, the relation between the exergy loss of the cell and the cell voltage is also shown. In these calculations, the current efficiency of a fuel cell or the loss of reactants in the conversion system was neglected, since these factors had only a small effect. The relationship between the exergy efficiency and cell voltage of the present model is given by Eq. (6). Therefore, it is found that the cell voltage over 0.82 V is necessary in order to obtain an exergy efficiency of more than 0.5. The exergy efficiency of a modern power station using the advanced gas turbine system has reached 0.5. A fuel cell system for vehicles will need this exergy efficiency to overcome the well to wheel efficiency compared to the conventional engine system. The fuel cell system will hopefully overcome this value in the near future.

At 80 °C, the maximum enthalpy efficiency becomes 71.6%. Using Eq. (6), the maximum exergy efficiency of the methanol reforming PEFC, which does not utilize the waste heat of the cell is calculated to be 72.2%, because the theoretical cell voltage is 1.189 V. However, the maximum exergy efficiency when recovering all the waste heat from the cell becomes 74.8%. The difference between these values is very small. In the methanol reforming PEFC system, the increase in a cell voltage is very important for increasing the exergy efficiency. The increase in heat recovery is effective for improving the enthalpy efficiency.

4.4. Comparison with the direct methanol fuel cell (DMFC)

A high exergy efficiency is theoretically expected for DMFC compared with the methanol reforming PEFC. The
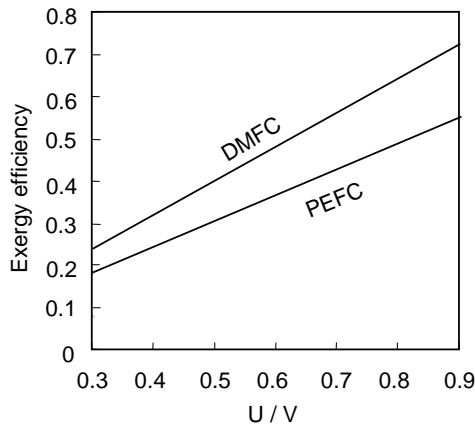
Fig. 8. Comparison between PEFC and DMFC.

DMFC system does not have a reforming system or a fuel treatment system, which means a much simpler system compared to the reforming PEFC. Each unit of a system has the possibility of decreasing the enthalpy or exergy efficiency. However, the irreversibility of the methanol reaction might be a major problem for DMFC using the present technology.

The relationship between the cell voltage of the PEFC, DMFC and exergy efficiency is shown in Fig. 8. The operating temperature of the DMFC was also fixed at 80 °C. The waste heat from the cell was not recovered in either case. The loss of current or reactant was not counted in either case. The difference in slopes between the two straight lines was based on the difference in the hydrogen utilization of the PEFC system. The difference between the DMFC and PEFC systems in exergy efficiency is mainly due to the exergy loss for the methanol reforming process. The theoretical exergy efficiency of the DMFC is higher than that of PEFC by about 0.1–0.15. However, it is necessary to consider the overvoltage at the actual measured cell voltage. The cell voltage of a present PEFC is about 0.65 V at 600 mA/cm^2, and it is about 0.40 V in a DMFC at 400 mA/cm^2 [10,11]. Therefore, the overvoltage of a DMFC is far greater than that of a PEFC. Using these actual cell voltages, the exergy efficiencies of the PEFC and DMFC systems become 39 and 32%, respectively. Therefore, the exergy efficiency of a PEFC is proved to be higher than that of a DMFC even if the exergy loss by the methanol reforming is large. If the current loss by the permeation of methanol through a membrane was counted, the difference would become even greater. It is also apparent that over 0.50 V is at least needed as the cell voltage by comparing them at 600 mA/cm^2 in order to have the exergy efficiency in which DMFC is higher than that of present methanol reforming PEFC.

5. Conclusions

A methanol reforming PEFC was modeled, and the efficiency of the system was analyzed using enthalpy and exergy. The following results were obtained.

1. The total exergy loss except for the fuel cell in this methanol reforming PEFC system was 193 kJ/mol MeOH. In other words, there was 193 kJ exergy loss for the steam reforming process of the methanol.
2. The enthalpy efficiency and exergy efficiency in the present model became a function of the cell voltage U (V), and they were 60.2U% and 60.7U%, respectively, when the waste heat recovery and the current efficiency were neglected.
3. The enthalpy efficiency approached unity as the recovery rate of the waste heat from the cell approached unity. However, the maximum exergy efficiency reached only 0.45, even if all the waste heat of the cell were recovered.
4. The relationship between the exergy efficiency and the cell voltage of the present model can be described as the following equation:

   exergy efficiency = 0.61 × cell voltage (V)

5. The DMFC and methanol reforming PEFC systems were compared using the exergy analysis. It was clarified that over 0.50 V was necessary as a cell voltage at 600 mA/cm^2 in order to have higher exergy efficiency in the DMFC than that in a methanol reforming PEFC using the current technology.

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