COMPARISON OF SYSTEM EFFICIENCY BETWEEN SOFCs FOR COMPACT COGENERATION AND PEFCs

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ABSTRACT

For applying SOFCs to compact cogeneration systems for domestic use, performance of SOFC systems operated at medium temperature (mtSOFC) with methane was investigated and compared with that of PEFC systems with a partial oxidation reactor (POX) which are being developed rapidly as small power units. Simple models were chosen for both systems in order to clarify the characteristics of these systems. The dependence of overall system efficiency on the components and the operating condition was analyzed. From the analysis, it was clarified that even if cell efficiency of mtSOFC is lower than that of PEFC, system efficiency of mtSOFC can be larger than that of PEFC.

INTRODUCTION

For the global environmental protection and conservation of fossil fuels, new types of power generators with high efficiency and low emission have been studied as the alternatives to internal combustion engine. Fuel cells are prospective candidates as the alternatives because of high efficiency and no emission of air pollutants. For compact cogeneration systems and automobiles, PEFCs operated at low temperature (80°C) have been developed world wide and excellent performance achieved by using hydrogen. Since hydrocarbons are more convenient as fuel for practical use, efforts are being focused on removing carbon monoxide in the synthesis gas without lowering system efficiency and developing PEFCs with durability against carbon monoxide. So far SOFCs have been developed for stationary power plants because of generation of high temperature heat and long start-up time attributed to their high operating temperature of 1000°C. However, since SOFCs have high fuel reforming performance and carbon monoxide can be used as fuel, improving the start-up time, and power weight and volume ratios make SOFCs favorable for the small power units also.

From this point of view, we have started investigating the potential of tubular SOFC systems. We concentrate our effort on the following two points.
1. Decreasing operation temperature.
2. Thinning substrate tubes.
By decreasing operating temperature, it may be possible to shorten the start-up time and to prolong the lifetime of the cells. Moreover, at low operating temperatures, metallic porous substrates with high mechanical strength can be used. Applying metallic components leads to large reduction in the weight and the cost of stacks. Furthermore, large improvement of the power weight and volume ratios is expected by thinning metallic substrate tubes. Ideally, power density of the stack composed of the thin tubes of 0.8 cm diameter whose average power density is 0.2 W/cm² reaches more than 500 kW/m³.

For decreasing operating temperature, Sm₂O₃ or Gd₂O₃ doped CeO₂, Sc₂O₃ doped ZrO₂ (1) and LaGaO₃ (2) are popular as the alternatives to the YSZ electrolyte. Several groups have reported high power density at medium operating temperatures (500°C ~ 800°C) by using ceria based electrolyte (3-6). However, since this electrolyte also has electronic conductivity, its electric conversion efficiency is lower than conventional SOFCs. The electric efficiency for an SOFC using CeO₂ electrolyte was estimated at 30 ~ 40% (HHV H₂) with hydrogen (7). Generally these values are low compared with the efficiency of PEFCs, but, in the case of hydrocarbon fuels, a reformer system increases the efficiency of a SOFC system and on the contrary decreases that of PEFC systems.

Therefore, in this paper, to study the possibility of applying SOFCs to compact cogeneration systems, performance of SOFC systems operated at medium temperature (mtSOFC) is estimated and compared with that of PEFC systems. Methane is considered as fuel. Simple process models are chosen to clarify the characteristics of these systems.

**MODELING**

Fig. 1 shows schematic diagrams for both fuel cell systems. The SOFC system consists of a cell unit, a steam reformer (SR), a combustor, heat exchangers (HEs) and a heat recovery system (HR). The PEFC system is composed of a cell unit, a partial oxidation reactor (POX), a high temperature shift reactor (HTS), a low temperature shift reactor (LTS), a combustor, HEs, HRs, and so on.

In the SOFC system, air utilization is fixed at 4%. Operating temperatures of the steam reformer and the cell unit are set at the same temperature. Steam to carbon ratio (s/c) in the fuel gas is chosen to prevent carbon deposition in the SR. The condition of carbon deposition is decided from hypothetical carbon activity, \( a_c \), calculated by following equations:

\[
a_c = K \frac{[H_2]^3}{[CH_4]} \quad [1]
\]

where \( K \) is an equilibrium constant of following reaction,

\[
CH_4 \rightarrow C + 2H_2 \quad [2]
\]

It is assumed that carbon is deposited when \( a_c \) is more than 1. Composition of reformed gas is calculated on the basis of thermodynamic equilibrium conditions (8).

Electric energy \( W \), heat \( Q \) generated in the SOFC unit, and system efficiency, \( \eta_{sys} \) are expressed as

\[
\Delta H = H_{out} - H_{in} \quad [3]
\]
\[ W = \eta_{\text{cell}} \left\{ (\text{mH}_2\text{in} - \text{mH}_2\text{out}) \Delta H_{\text{H}_2}(298) + (\text{mCO}_{\text{in}} - \text{mCO}_{\text{out}}) \Delta H_{\text{CO}}(298) \right\} \]  
\[ Q = -\Delta H - W \]  
\[ \eta_{\text{sys}} = \frac{w}{\Delta H_{\text{CH}_4}(298)} \]

where, \( H_i, \text{mH}_2i, \text{mCO}_j \) are enthalpy of the gas, number of moles of hydrogen and carbon monoxide at the location i, respectively. Subscript “in” and “out” denote the inlet and the outlet of the SOFC unit. \( H_{\text{out}} \) and the composition of the outlet gas are also calculated from the equilibrium conditions. \( \Delta H_{\text{H}_2}(T), \Delta H_{\text{CO}}(T), \Delta H_{\text{CH}_4}(T) \) are heat of combustion of hydrogen, carbon monoxide and methane at temperature T. These values are calculated on the basis of the high heat values (HHV). \( \eta_{\text{cell}} \) is the control parameter and denotes electric efficiency of a fuel cell operated with hydrogen on the basis of HHV.

Methane in the reformed gas is assumed to be converted into carbon monoxide and hydrogen at the inlet of the SOFC unit at the conversion efficiency of \( \varepsilon \).

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

There are many proposals of the rate equation for the conversion of methane in a SOFC (9). However, since it is not clear that they are adequate for mtSOFC, \( \varepsilon \) is adopted as a control parameter instead of using the rate equation. Residual methane is consumed in the combustor. Hydrogen and carbon monoxide are assumed to be consumed in the SOFC unit at the utilization of \( \eta_{\text{H}_2\text{CO}} \). The influence of change of gas concentration in the fuel cell on the output power is neglected.

The PEFC system is treated in a similar way. The operating conditions of reforming components are decided on the basis of data reported by several groups (10-12). Composition of the reformed gas is assumed to be kept constant from POX to HTS and from HTS to LTS. In the two shift reactors only water shift reaction is considered as the reaction (10). All carbon monoxide is assumed to be removed at the outlet of LTS. Other assumptions for this analysis are the following:

1) Reactions in the combustors, POX, HTS and LTS are adiabatic.
2) Reactions reach equilibrium in SR, POX, and both fuel cell units.
3) Pressure drop and heat loss over the various components of both systems are neglected.
4) Heat recovery systems control the heat balance between reactants and products automatically.

RESULTS AND DISCUSSION

SOFC System

Fig. 2 shows dependence of carbon activity on the operating temperature and s/c. Although carbon activity in the medium temperature region is high compared with high temperature region (higher than 1000K), s/c of 1.5 is enough to avoid carbon deposition within thermodynamical equilibrium conditions. Then, in this paper s/c is considered to be greater than 1.5. For s/c of 2, change of the composition of reformed gas and endothermic heat of

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steam reforming with temperature is shown in Fig. 3 and Fig. 4, respectively. Reforming rate of methane is almost 100% at more than 1000K but it decreases to 41% at 800K. Hence, in the medium temperature region, conversion rate, $\varepsilon$ becomes an important factor for the electrical energy output. For $\varepsilon$ of 0.75, dependencies of electric energy and heat generated at the SOFC on the operating temperature are shown in Fig. 5. Both outputs decrease with decreasing operating temperature, the heat output can be recovered by using combustor. On the other hand, for electric energy, decreasing operating temperature is critical. In this case, if the operating temperature is decreased from 1000K to 800K, electric energy decreases about 15%. Although the output is increased slightly with increasing s/c, this improvement is not enough to recover it. At the operating temperature of 1000K, for the cell efficiency of 40%, reformer increases system efficiency to approximately 46%, on the contrary, at 800K system efficiency decreases to 38%. This value is lower than cell efficiency. Therefore, It is very important for development of mtSOFC to improve conversion rate $\varepsilon$.

**PEFC System**

Fig. 6 shows the composition of reformed gas in the POX for the oxygen to methane ratio (o/c) of 0.5. The mole fractions of hydrogen and carbon monoxide increase with temperature and methane is almost converted (mole fraction of 0.1%) into hydrogen (39.8%) and carbon monoxide (19.9%) at 1300K. Further, exothermic heat of this reaction decreases to 22.3kJ/(1mol CH$_4$) at 1300K (Fig.7). Actually similar data were reported for hydrocarbon fuels(11). However, as shown in Fig.8, since carbon activity becomes much higher than 1 at the temperature below 1200K, it may be necessary to prevent carbon deposition.

With the temperature of the HTS and LTS fixed at 700K and 400K (10,12), s/c is optimized to give maximum conversion of carbon monoxide to hydrogen in the LTS. Fig.9 shows the dependence of composition of reformed gas in the LST on the s/c. Optimum value of the s/c is found to be 1. At this value, 49.1% of hydrogen and 0.08% of carbon monoxide are produced in LTS. Moreover, the heat of reaction generated in HST and LST is 22.6kJ/(1mol CH$_4$) and 14.5kJ/(1mol CH$_4$) respectively. Under these optimum conditions, the relationship between system efficiency and cell efficiency is shown in Fig. 11. In this case, system efficiency results in 84% of cell efficiency for fuel utilization, $U_f$ of 90%.

**Comparison Between SOFC System and PEFC System**

For both systems the relationships between enthalpy of the system and the temperature are shown in Fig.10. In the PEFC system, even if its reforming system is under the optimum conditions, heat of 59.4kJ is produced in POX, HTS and LTS. This value corresponds with 6.7% of $\Delta H_{\text{fus}}$(298). Therefore, system efficiency decreases slightly from cell efficiency. On the other hand, in the SOFC system, if conversion rate of methane in SR is 1, endothermic reaction of reforming increases system efficiency. Fig.11 also shows relationship between SOFC system efficiency and the cell efficiency for several operating temperatures. Since the reforming rate at 1000K is almost equal to 1, the system efficiency reaches approximately 110% of cell efficiency. Therefore when the cell efficiency of the SOFC is 76% of that of the PEFC, both systems have the same system efficiency. However, as mentioned above, with decreasing reforming temperature, reduction of SOFC system efficiency is caused by decreasing reforming rate. At 800K, cell efficiency of SOFC must be increased to 83% of that of PEFC to obtain the same system efficiency.
CONCLUSIONS

As a result of this analysis, following can be concluded:

1. Conversion rate of methane included in reformed gas is one of the key factors for developing mtSOFC.

2. Even if cell efficiency of mtSOFC is lower than that of PEFC, system efficiency of mtSOFC can be larger than that of PEFC by utilizing endothermic heat of reforming reaction effectively.

3. The performances of component elements of mtSOFC systems needs to be improved to optimize the performance of mtSOFC systems.

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Fig. 1. Schematic diagrams of a SOFC system and a PEFC system.

Fig. 2. Carbon activity of the reformed gas in the steam reformer.
Fig. 3. Equilibrium composition of steam reformed gas.

Fig. 4. Endothermic heat of steam reforming.

Fig. 5. Electric energy and heat generated in the SOFC.
(a) Electric energy  (b) Heat output
Fig. 6. Equilibrium composition of reformed gas in POX.

Fig. 7. Change of enthalpy of the reaction in POX.

Fig. 8. Carbon activity of the reformed gas in the POX.

Fig. 9. Equilibrium composition of reformed gas in LTS.
Fig. 10. Changes of enthalpy in the SOFC system and the PEFC system.

Fig. 11. Comparison of system efficiency between SOFC and PEFC.