DESIGN OF ENERGY AND CHEMICALS CO-PRODUCTION SYSTEMS USING SOLID OXIDE FUEL CELL TECHNOLOGY

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ABSTRACT

Electrochemical partial oxidation of methane by a SOFC is simulated and investigated as an application to energy and chemicals co-production system. Effect of SOFC operation temperature on electric power generation, the yield of products, and the capability for upgrading the quality of energy is examined. Under the conditions considered, a SOFC operated at 1273 K exhibited the maximum electric power of 0.60 W/cm² at the average current density of 1.2 A/cm² with the synthesis gas selectivity of 62%. The ratio of the generated electric power to the enthalpy change determined from methane conversion is larger than 1, indicating the feasibility of energy upgrading from thermal energy to electricity.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have attracted much attention since they can achieve high thermal efficiency due to their high operating temperature. Integrated system of a gas turbine with SOFC as the combustor has been proposed for large-scale power generation and the thermal efficiency of such systems has been evaluated. In such systems, electrochemical oxidation of fuel such as methane occurs in a SOFC reactor to generate electricity and high temperature combustion gas simultaneously to drive a gas turbine. Consequently, enthalpy and Gibbs free energy change of the oxidation reaction are effectively converted to electricity, resulting in high thermal efficiency. Havey and Richter analyzed thermodynamically a gas turbine power generation cycle integrated with SOFC and estimated the thermal efficiency of the cycle (1). They reported that by replacing the combustion chamber with SOFC, the thermal efficiency improved by about 10% based on the lower heating value (LHV) of methane and the optimized cycle with methane steam-reforming achieved a thermal efficiency of 68.1 and 77.7% (LHV) in the case with/without major losses, respectively. Tanaka et al. evaluated a high-pressure combined system with SOFC and gas turbine based on total electricity generation efficiency and cost/energy payback times (2). Their proposed system including major component losses, operated at a working temperature and pressure of 1073 K and 0.4 MPa, exhibited the efficiency of 68.3% with cost payback time = 9.3 years and energy payback time = 0.71 years.
Recently, new applications of SOFCs as a chemical reactor have been suggested for chemicals and energy co-production and demonstrated experimentally (3,4,5). These applications utilize SOFC as a membrane through which oxygen permeates for selective oxidation of reactants on the anode and the Gibbs free energy change in the reaction can be converted to electric power, leading to realization of efficient chemicals and energy co-production systems. Tagawa et al. investigated experimentally ethane and ethene production with electric power by methane oxidation in a SOFC reactor (3,4). They prepared LaAlO anode catalyst and observed co-generation of electricity and C2 compounds with high selectivity. Ishihara et al. carried out partial oxidation of methane by using LaGaO3-based perovskite as electrolyte and showed that large electric power, CO-H2 mixture with H2/CO ratio equal to 2, and heat energy were produced simultaneously (5). Fe-doped LaGaO3, 0.5 mm thick, exhibited a maximum power density of 731 mW/cm2 with synthesis gas yield of 21% at 1273 K. As these works experimentally proved, valuable chemicals and electric power can be generated simultaneously in SOFC type reactors, indicating that a high efficiency energy and chemicals co-production system is feasible by using SOFCs.

Another beneficial feature of carrying out reaction electrochemically with SOFCs is the possibility to absorb heat and transform it to electric power, that is, to upgrade the quality of energy. Exothermic reactions in which entropy change is positive are capable of converting absorbed heat into electric power if such reactions proceed electrochemically in SOFC reactors. Partial oxidation of hydrocarbons, regarded as a valid method of on-site hydrogen production for fuel cells (e.g. (6)), belongs to this type of reactions. Normally, partial oxidation of hydrocarbons is brought about by direct contact with air, which makes no use of the capability for the energy upgrading and gives rise to reduction in energy utilization. In this study, therefore, partial oxidation of hydrocarbons in a SOFC reactor is analyzed and evaluated thermodynamically as an efficient energy and chemicals co-production system. Effects of reaction temperature and cell voltage on the performance of the systems are examined.

THERMODYNAMICAL ANALYSIS

When evaluating energy conversion processes, it is important to determine the efficiency of energy utilization by considering both the first and the second law of thermodynamics, because enthalpy change and degradation of energy quality take place simultaneously during energy conversion processes. The concept of exergy is useful to assess the quality of energy and to find an inefficient process in a system. The basic exergy expression is defined as follows:

\[ \varepsilon = (H - H_0) - T_0(S - S_0) \]  

where \( H \) and \( S \) denote enthalpy and entropy at temperature \( T \), respectively, and subscript 0 refers to the reference condition, chosen as ambient condition at 298.15 K, 101.3 kPa for this study. This basic expression \([1]\) is similar to that of Gibbs free energy. The difference lies in that work is needed to obtain heat energy at temperature \( T \) when considering exergy at \( T \), while heat energy at \( T \) is available without work in Gibbs free
energy consideration.

To judge efficiency for an energy conversion process, an energy conversion diagram proposed by Tsutsumi (7) is useful. This diagram illustrates the change in the rate of exergy to enthalpy during a conversion process into heat, electric power and chemicals. The exergy rate to enthalpy represents the quality of energy, that is, the fraction of the total energy convertible into work such as mechanical and electrical power. The energy conversion diagram for partial oxidation of methane, \( \text{CH}_4 + l/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \), is displayed in Fig. 1(a) and (b) in the case of direct and electrochemical oxidation, respectively. This reaction is associated with exergy and enthalpy change from 818 kJ/mol to 731 kJ/mol and from 890 kJ/mol to 854 kJ/mol, respectively. Methane with exergy rate of 92% is converted into a mixture of CO and H\(_2\) possessing exergy rage of 86%. Thus, direct partial oxidation of methane loses exergy of 87 kJ/mol and enthalpy of 36 kJ/mol if no heat recovery is achieved. Even with full recovery of the enthalpy loss, if recovered at 1073 K as denoted by the dotted line in Fig. 1(a), only 18 kJ/mol is regained as exergy because thermal energy has exergy rate close to 0.5 at 1073 K. Therefore, direct methane partial oxidation results in exergy loss of about 10%, namely, reduction in the energy quality. Figure 1(b) depicts electrochemical partial oxidation of methane performed at 1073 K. Besides the production of CO and H\(_2\), exergy change in the reaction is transformed to electric power that has exergy rate of 1. As indicated by the dotted line in Fig. 1(b), thermal energy is absorbed since exergy change is larger than enthalpy change in this case. This is clearly elucidated in Fig. 2 that describes G-T diagram for a reaction with \( \Delta H < 0 \) and \( \Delta S > 0 \). This type of reactions can absorb heat corresponding to the difference \( \Delta H - \Delta G \), as schematically represented in Fig. 2. As a result, it is possible to upgrade the quality of energy from heat with exergy rate less than 1 into electric power with exergy rate of 1, if the reaction proceeds electrochemically. In total, exergy as well as enthalpy are conserved as shown in Fig. 1(b), demonstrating no decrease in energy quality occurs during electrochemical partial oxidation.

\[ \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2 \]

\[ \Delta H = 818 \text{ kJ/mol} \]

\[ \Delta S = 890 \text{ kJ/mol} \]

\[ \text{Exergy} = 92\% \]

\[ \text{Enthalpy} = 36 \text{ kJ/mol} \]

\[ \text{Electric power} = 138 \text{ kJ/mol} \]

\[ \text{Process coordinate} = 298 \text{ K} \]

Fig. 1, Energy conversion diagram of methane partial oxidation: (a) direct oxidation, (b) electrochemical oxidation.
As described above, the energy conversion diagram exemplifies the advantage in carrying out reactions with $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$ electrochemically. Nevertheless, since the diagram assumes ideal conditions, we examine the applicability of SOFCs to efficient energy and chemicals co-production by setting up a SOFC model in the following sections.

Fig. 2, Schematic representation of G-T diagram for reaction with $\Delta H^\circ < 0$, $\Delta S^\circ > 0$.

SOFC MODEL

A planar type SOFC of a single-cell layer is simulated in the present work, which is considered to be placed deep enough within a SOFC stack so that the end effects may be neglected. A simplified single-unit cell with air and fuel co-flow as depicted in Fig. 3 is modeled by referring to the work by Ahmed et al. (8) with the assumptions as follows: (a) pressure drop in the flow direction is neglected, (b) overpotential is neglected, (c) temperature of fuel and air is uniform along the cell, (d) all reactions in the gas phase are in equilibrium, (e) heat is released or absorbed only in the electrolyte layer, (f) the cell is thermally insulated, thereby heat transfer occurs only between the solid fuel cell component and the air and fuel streams, (g) the SOFC is in a stationary condition, that is, time independent. All results presented here are obtained using Aspen Plus process simulation software (Aspen Technology Inc.) in conjunction with the SOFC cell model we developed as an external Fortran subroutine. The simplified cell is divided into 100 segments in the flow direction, and subsequently electrochemical reaction scheme as well as steady-state heat and mass transfer equations are set up for each segment.

Electrochemical Reaction Scheme

To specify the reactions taken into account, the conversion of methane partial oxidation is calculated based on thermodynamic equilibrium conditions. The equilibrium composition calculation is carried out for a constant $\text{CH}_4/\text{O}_2$ molar ratio at various reaction temperatures of 773 to 1373 K under 101.3 kPa. Components such as $\text{O}_2$, $\text{CH}_4$, $\text{CO}$, $\text{CO}_2$, $\text{H}_2$, $\text{H}_2\text{O}$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, and $\text{C}_3\text{H}_8$ are included in the thermal equilibrium calculation. Figure 4 shows the calculation result: the amount of $\text{O}_2$, $\text{C}_2\text{H}_6$, and $\text{C}_3\text{H}_8$ is negligible over the temperature range, hence the results for these components are excluded from the figure. It can be seen in Fig. 4 that the gas composition in the chemical equilibrium reached by partial oxidation of methane consists mainly of $\text{CH}_4$, CO and $\text{H}_2$ under the conditions examined. The molar ratio $\text{H}_2$:CO is close to 2 in the...
chemical equilibrium. Furthermore, between 950 and 1200 K the amount of CO2, H2O and C2H4 is found to be almost zero. Consequently, the product of methane partial oxidation can be limited to CO and H2, and the following reactions are thus considered in this simulation.

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2
\]  

[2]

The Nernst potential at segment \(i\) is determined from the equation,

\[
E_i = -\frac{\Delta G_r(T_f)}{nF} + \frac{RT_f}{nF} \ln\left(\frac{P_{\text{CH}_4,\text{av}}}{P_{\text{O}_2,\text{av}}^{0.5}}\right)
\]

[3]

where \(\Delta G_r\) represents the Gibbs free energy change of methane partial oxidation at the fuel stream temperature \(T_f\), and partial pressure for each compound is the average value of the pressure at the segment inlet and outlet, denoted with subscript \(\text{av}\). The total resistance at segment \(i\), \(R_i\) is calculated from the resistivities of the individual layers. Constant resistivities are adopted for the anode and cathode layers (0.0014 and 0.0186 \(\Omega\)-cm, respectively), whereas the resistivity of the electrolyte layer is assumed to depend on the electrolyte temperature \(T_{e,i}\) according to the following relationship, \(0.3865 + 0.002838\exp(10300/T_{e,i})\) (\(\Omega\)-cm). In addition, anode and cathode interfacial resistances, both of which are 0.10 \(\Omega\)-cm\(^2\), are included. As a result, the current generated at segment \(i\) is expressed for a cell voltage \(V\) as follows:

\[
I_i = \left(\frac{E_i - V}{R_i}\right)
\]

[4]

**Heat and Energy Balance**

Heat is generated in the segment from the resistance to current flow and from the entropy change of the electrochemical reaction. The total heat released \(Q_i\) is given by

\[
Q_i = \frac{I_i}{nF}(-\Delta H_r(T_f)) - VI_i
\]

\[
= I_i^2 R_i + \frac{I_i}{nF}(-\Delta H_r(T_f) + \Delta G_r(T_f))
\]

\[
= I_i^2 R_i + \frac{I_i}{nF}(-T_f \Delta S_r(T_f))
\]

[5]

By assuming convective heat transfer between the SOFC component and the flowing air and fuel streams and isothermal condition for the air and fuel streams, the heat transfer and energy balance equations are set up for the segment using the fuel and air side heat transfer coefficient, \(h_f\) and \(h_a\), respectively,

\[
Q_i - Ah_{f}(T_{e,i} - T_{a}) - Ah_{f}(T_{e,i} - T_{f}) = 0
\]

[6]

\[
G_{i;C_{p,a}}(T_{a} - T_{a}) - G_{i;C_{p,a}}(T_{a} - T_{a}) + Ah_{a}(T_{e,i} - T_{a}) = 0
\]

[7]

\[
F_{i;C_{p,f}}(T_{f} - T_{a}) - F_{i;C_{p,f}}(T_{f} - T_{a}) + Ah_{a}(T_{e,i} - T_{a}) = 0
\]

[8]
Fig. 3, Schematic diagram for single-layer SOFC with co-flowing air and fuel streams used in the simulation.

where $A$ is the heat transfer area (1 mm$^2$), $G$ and $F$ represent air and fuel flow rate, respectively, $C_p,a$ and $C_p,f$ stand for the heat capacity of air and fuel at constant pressure, respectively. The heat transfer coefficients are calculated by adopting Nusselt number of 3.0 and the equivalent diameter of rectangular flow channels. To obtain the model solution from the equations defined above, inlet, outlet and average conditions within a segment are needed. However, because the outlet and thus average conditions are unknown at the beginning of calculation, an iteration scheme is used to converge on the segment outlet and average values.

RESULTS AND DISCUSSION

In the present work the anode inlet flow consists of 100% methane flowing at $1.0 \times 10^{-5}$ mol/s and the cathode inlet flow is air with 79% nitrogen and 21% oxygen at a flow rate of $4 \times 10^{-4}$ mol/s. The SOFC is operated at 101.3 kPa and the temperature of the anode and cathode flows is varied from 1073 to 1273 K. Figure 5 shows the current density...
and Nernst potential distribution along the cell. The results presented in Fig. 5 are obtained for the cell voltage of 0.6 V and the temperature of 1273 K. Both the Nernst potential and current density are large near the fuel inlet, and subsequently drop off rapidly to a stable value. In the proximity of the fuel inlet the partial pressure of CO, H₂ is low and accordingly the resultant Nernst potential determined from equation [6] is high near the inlet. The variation of electrolyte temperature and fuel and oxygen utilizations in the fuel flow direction is displayed in Fig. 6. The fuel and oxygen utilizations monotonically increase in the fuel flow direction. This monotonic increase in the fuel utilization means constant generation of current, which agrees with the constancy in the current density except at the inlet, as exhibited in Fig. 5. The electrolyte temperature rises steeply near the fuel inlet and becomes constant at around 1253 K. Since the temperature difference in the electrolyte is insignificant between the inlet and the successive part of the cell, the electrolyte resistance can be almost constant, leading to the similar profile of the Nernst potential and the current density shown in Fig. 5. The electrolyte temperature of the fuel cell unit is low compared to the temperature of the fuel and air streams, indicating heat transfer occurs from the streams to the electrolyte layer.

Figure 7 plots the electric power output and fuel and oxygen utilizations as a function of the current density averaged along the cell for the temperatures of 1073, 1173 and 1273 K. The fuel and oxygen utilizations are proportional to the average current density independent of the operation temperature. This result points out that the yield of synthesis gas increases consistently with the average current density. As the average current density increases, the power output increases initially and then reaches its maximum, and subsequently decreases with further increase in the current density. The power output becomes larger at an average current density as temperature is raised. In addition, the average current density, for which the power output takes its maximum, shifts toward the higher value as temperature increases, which means that the capability of chemicals and energy co-production can be enhanced by increasing SOFC operation temperature. The highest power output under the conditions examined is 0.60 W/cm² at the average current density of 1.2 A/cm² with the synthesis gas selectivity of 62%.

![Nernst potential and current density distributions in the flow direction.](image)

Fig. 5, Nernst potential and current density distributions in the flow direction.
Fig. 6, The variation of electrolyte temperature and fuel and oxygen utilizations in the flow direction.

Fig. 7, Effect of average current density on power output and fuel and oxygen utilizations for the temperatures of 1073, 1173 and 1273 K.

The computed ohmic heat and heat released according to equation [5] are shown in Fig. 8. The amount of heat released according to equation [5] is negative for all of the cases analyzed in the present work. It is, therefore, demonstrated that thermal energy can be absorbed and transformed into electric power by carrying out partial oxidation of methane electrochemically in a SOFC type reactor. For an averaged current density the amount of heat absorbed increases with reaction temperature. This is attributable to combined effects as follows: 1) the electrolyte resistance decreases with temperature, leading to reduction in ohmic loss, 2) the capacity for absorbing heat, $T\Delta S$, increases with temperature.
Fig. 8, Effect of average current density on ohmic heat and heat released in electrolyte for the temperatures of 1073, 1173 and 1273 K.

Fig. 9, Power generation efficiency for Gibbs free energy change based on methane conversion.

Figure 9 shows the electric power generation efficiency for Gibbs free energy change based on methane conversion. For all temperatures, the generation efficiency decreases linearly with average current density. This reduction can stem from the ohmic loss increasing with the current density as represented in Fig. 8. The largest power generation efficiency based on $\Delta G$ results in at most 60%.

Figure 10 represents the ratio of power output to the enthalpy change calculated on the basis of methane conversion. Though the ratio decreases as the average current density increases, it takes values larger than 1 for the cases analyzed. This result demonstrates
the feasibility that the thermal energy larger than the enthalpy change of the reaction [2] is absorbed and transformed into electric power by using SOFC type reactors, as suggested by the thermodynamic analysis. It can be concluded that since the decrease in the conversion efficiency due to ohmic heat is significant for high current densities, it is important to use materials with high conductivity for highly efficient energy and chemicals co-production systems.

SUMMARY

A mathematical model for SOFC is set up to examine the applicability of SOFCs to energy and chemicals co-production. Partial oxidation of methane to produce CO and H₂ is simulated and it is demonstrated that the maximum power output of 0.60 W/cm² is obtained at operation temperature of 1273 K and the current density of 1.2 A/cm² with the synthesis gas selectivity of 62%. It is also demonstrated that SOFC type reactors can absorb thermal energy and convert it to electric power by carrying out a reaction with $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$. Further work is necessary to evaluate the energy and chemicals co-production as a system and to find optimum operating conditions.

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