EVALUATION OF A SOLID OXIDE FUEL CELL AND GAS TURBINE COMBINED CYCLE WITH DIFFERENT CELL COMPONENT MATERIALS

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ABSTRACT

A system model integrating a solid oxide fuel cell and a gas turbine (SOFC/GT system) was constructed. Based on the constructed model, we have carried out comprehensive evaluations of various candidate materials for SOFC cell components. An optimization study was carried out so that SOFC/GT system can achieve the highest efficiency at certain conditions. For the evaluation, a cathode supported tubular type cell was selected as cell structure, and operation temperature was set at 800°C. We have optimized the system for several sets of cathode/electrolyte/anode materials. System cost and efficiency were obtained for each set of cathode/electrolyte/anode materials as a result of the optimization. SOFC/GT system using yttria stabilized zirconia electrolyte turned out to be economically competitive at the operation temperature of 800°C although further lowering of overpotentials are needed to achieve higher output power density. Evaluations carried out for several candidate materials for SOFC cell components indicated the suitable materials for the construction of a low cost system. Several methods for lowering the system cost were also evaluated. The constructed model can be used as a platform for comprehensive evaluation of various candidate materials for SOFC cell components.

INTRODUCTION

Solid oxide fuel cell (SOFC) is expected to be one of the promising technologies to mitigate the global warming. However, several issues, such as long-term stability, high system cost, high operation temperature and reliability, need to be solved before
successful introduction of SOFCs into our society on a large scale. Tanaka et. al. have carried out evaluation of the SOFC/GT system (1). The constructed model made clear the SOFC/GT system’s capability of system efficiency about 70%. The model also clarified the suitable operation conditions, and further necessity of lowering the overpotentials at intermediate temperatures for higher system efficiency. In selecting materials for SOFC, we have to evaluate the materials from various viewpoints, i.e. material cost, manufacturing cost, electrical property, catalytic property, long term stability, thermal stability, thermal expansion property, chemical compatibility between materials and so on. Therefore, it is quite complex to estimate most suitable set of cell component materials for practical SOFC. Toward this need of comprehensive evaluation of cell component materials, we have tried to evaluate the cell component materials in the context of SOFC/GT system. By carrying out the evaluation in the context of SOFC/GT system, we can evaluate several properties of cell component materials, which influences the system efficiency, cost, etc., at the same time.

**SOFC/GT SYSTEM**

**Background**

SOFC/GT system used in this manuscript was based on the model constructed by Tanaka et. al. (1). The considered SOFC/GT system consists of a pressurized SOFC system, combustion turbine, air/fuel compressors, generator and sub assemblies such as control panel, reduction gear, inlet-outlet ports and piping for the GT system. Figure 1 shows a schematic diagram of the SOFC/GT system. The SOFC system considered here is composed of SOFC modules, an AC-DC inverter, transformer, insulation materials, pre-heating heat exchangers, piping, and pressure vessel. A cathode supported tubular cell was selected as the cell structure. Thickness of the cathode, electrolyte and anode is 2, 0.02 and 0.1 mm, respectively. The relative density of cathode, electrolyte, anode is 70, 97 and 60 %, respectively. Further details about the configuration of cell and SOFC module are described elsewhere (1). Total plant lifetime was assumed to be 20 years, and SOFC cells, catalysts and main bodies of GT were changed every five years. System investment cost and CO₂ emissions were calculated based on the weight of the materials used in the system. In this manuscript, we have carried out evaluations by changing the cell component materials of SOFC/GT system.

Fig. 1 Schematic diagram of SOFC/GT system
Improvement of the Model

In order to evaluate the effect of cell component materials on the system efficiency and cost, we have changed the method of the cost estimation of cell component materials. We have adopted the results of cost estimation for SOFC by Ippomatsu et. al. (2) only for the estimation of manufacturing cost of a single cell. The annual production rate of one million cells per plant was assumed in the estimation. The unit cost of each cell component material is determined based on the industrial cost as shown in 13700 Chemical Products (3) complemented with inquiries to material manufacturers and so on. The cost of raw materials used in this manuscript is shown in Table 1. Here the cost of GT and heat exchanger was reexamined using the new commercial product data.

Table 1 List of raw material cost

| Compounds | Cost (¥/kg) | Compounds | Cost (¥/kg) |
|-----------|-------------|-----------|-------------|
| MgO       | 300         | BaCO$_3$  | 200         |
| MnO$_2$   | 160         | Y$_2$O$_3$| 7300        |
| Fe$_2$O$_3$| 200         | ZrO$_2$   | 2200        |
| Co$_3$O$_4$| 1700        | La$_2$O$_3$| 2300        |
| NiO       | 1000        | CeO$_2$   | 3400        |
| Ga        | 65000       | Sm$_2$O$_3$| 4500        |
| SrCO$_3$  | 650         | Gd$_2$O$_3$| 6000        |

EVALUATION

Cell Component Materials for Evaluations

We have selected four kinds of electrolytes for the evaluations. They are 8-YSZ, SDC (Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$), BCG (BaCe$_{0.6}$Gd$_{0.4}$O$_{3}$), and LSGM (La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$). For each electrolyte material, we have selected chemically stable electrode material with low overpotentials as shown in Table 2. The system in which each electrolyte is used is abbreviated as YSZ-, SDC-, BCG-, and LSGM-system, respectively. The volume ratio of Ni in cermet electrode was kept at 40 %. Electrical properties and overpotentials are determined from the literature (5-12) and experimental results. The sums of

Table 2 Sets of component materials for evaluations

| cathode     | electrolyte | anode   |
|-------------|-------------|---------|
| YSZ-system  | LSM ((La$_{0.9}$Sr$_{0.1}$)$_{0.9}$MnO$_3$) | YSZ     | Ni-YSZ  |
| SDC-system  | SSC (Sm$_{0.5}$Sr$_{0.5}$CoO$_3$) | SDC     | Ni-SDC  |
| BCG-system  | La$_{0.6}$Ba$_{0.4}$CoO$_3$ | BCG     | Ni-BCG  |
| LSGM-system | SSC         | LSGM    | Ni-SDC  |

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overpotentials at electrode, electrolyte and interconnector for various systems are shown in Fig. 2. The ohmic loss at the electrode in the lateral direction occupies greater part of total overpotentials as reported in the previous work (1). The ohmic loss at electrode was lowered by using highly electronic conductive cathode (Doped LnCoO3) in the systems other than the YSZ-system. The influence of electronic conduction in reducing atmosphere and hole conduction in oxidizing atmosphere on electromotive force was considered only for SDC and BCG-system respectively, by adopting the Wagner's theory (4). The influence of exchange current on the anodic and cathodic atmosphere was neglected. The terminal voltages of each system are shown in Fig. 3. Although overpotential is lowest in the SDC-system, large influence of electronic conduction causes lowering of obtained voltage, which results in comparable terminal voltages to that of the YSZ-system.

![Fig. 2 Overpotentials for various systems](image1)

![Fig. 3 Terminal voltages for various systems](image2)

**Calculation Basis of Evaluation**

Influences of gas utilization ratio on overpotentials were considered only for the cathodic overpotentials, based on the $P_{O_2}$ dependencies of electrode resistances obtained from experiments (8-10). Physical properties except electrical property and electrocatalytic property, which determine overpotential, were not explicitly considered in this manuscript. All the cell components were assumed to be manufactured by sintering process. We also assumed that the cost for manufacturing process was the same for different cell component materials. All the evaluations were carried out at the conditions shown in Table 3. The distributions of current density, gas concentration and temperature are not explicitly

| Table 3 Operation conditions for evaluations |
|------------------------------------------------|
| Operation Temperature | 800 [°C] |
| Steam Carbon Ratio | 1.2 [-] |
| Fuel Utilization Ratio | 0.8 [-] |
| Air Utilization Ratio | 0.3 [-] |
| Operation Pressure | 4 [atm] |
| System Output Power | 1500 [kWe] |
| Fuel | Natural Gas |
considered. In this condition, we changed current density of the cell and optimized the system structure to achieve the highest efficiency for various sets of cell component materials for each current density.

**SYSTEM ANALYSIS**

**Evaluations of Standard Systems with Different Cell Component Materials**

First we carried out evaluation for the YSZ-system. Figure 4 shows the dependencies of system efficiency and system investment cost per unit output power on current density of the cell. At current density less than about 0.3 Acm\(^2\), the system efficiency achievable is almost the same. While at current density higher than 0.3 Acm\(^2\), the system efficiency decreases corresponding to the increase of overpotentials. The dependence of the system investment cost on current density shows the same tendency. The rapid decrease of the investment cost with the increase of current density at near 0.3 Acm\(^2\) can be seen in Fig. 4. This tendency is caused by the increase of the power density although the system efficiency decreases. Under the conditions that the exhaust heat is low, i.e. low overpotential conditions at a low current density, additional fuel is directly introduced into GT to enhance the temperature of turbine inlet gas, which is needed to achieve higher system efficiency. This introduction of additional fuel requires additional feed pipes and heat exchangers and causes cost increase at a low current density too. This additional cost could be avoided by lowering the fuel utilization ratio.

Herein, the electricity cost per kWh (EC) other than investment cost per kW as a cost indicator was also calculated using Equation [1].

\[
EC = \frac{Fuel\text{Cost} + Investment\text{Cost} + Annual\text{Expenditure}}{Operation\text{Rate}} + Labour\text{Cost} \quad [1]
\]

For the calculation, the annual expenditure for the fixed cost such as depreciation, maintenance, tax and interest costs was assumed to be 15\% of investment cost. The labor cost was assumed to be 1 ¥kWh\(^{-1}\). The EC of YSZ-system is shown in Fig. 5. The EC decreased as the current density increases. On the other hand, the EC showed the minimum value at the current density of about 0.4 Acm\(^2\) for the YSZ-system.

We have carried out evaluations, in the same way, for SDC-, BCG-, and LSGM-system, respectively. The results of these evaluations are shown in Fig. 5. The ECs for
SDC- and BCG-systems are almost the same as that of YSZ-system at the current density giving the minimum cost for each system. On the other hand, LSGM-system is cheaper than YSZ-system at the current density of 0.6 Acm\(^2\) because of higher output power density than that in YSZ-system. In LSGM-system, electricity cost begins to increase slightly at higher current density than 0.6 Acm\(^2\). The drastic change between 0.5 and 0.6 Acm\(^2\) occurs for the same reason for the change at around 0.3 Acm\(^2\) in the YSZ-system. The results indicate a possibility of constructing cheap systems even using materials containing expensive elements such as Ga and Sm by lowering the overpotentials, although the problem of scarcity of resources still exists.

The minimum EC for YSZ system is about 7 ¥kWh\(^1\), which seems competitive enough to be introduced into Japanese power grid. However, further lowering of EC is required for accelerated introduction into Japanese power grid or introduction into power grids of other countries in which EC is much cheaper than in Japan. Therefore, in the next section, we will examine several approaches to lower the cost of SOFC/GT system by changing the cell component materials and configurations of SOFC.

**Evaluations of Improved Systems**

**Thermal Efficiencies and Costs of Systems with Various Cathode Materials.** In order to clarify the difference of systems in which SOFCs are composed of different materials, we focused on YSZ- and SDC-systems and compared the systems in more detail. YSZ-system is considered as a base system for comparison and SDC-system is selected because the problem of material resources is not severe in this system. The investment costs for the two systems at the current density of 0.4 Acm\(^2\) are shown in Fig. 6. The difference in the investment cost of the two systems is mainly ascribed to the cost difference of cathode. Because cathode is used as support tube in this model, mass fraction of cathode is much larger than that of
other cell components. In SDC-system, SSC, which is much expensive than LSM, is used as cathode. Raw material cost per unit weight of Sm₂O₃ is twice as much as that of La₂O₃ and Co₂O₃ is ten times as expensive as MnO₂. Accordingly, substitution of La and Mn for Sm and Co respectively, seems to be effective for lowering the system cost. However, as is well known, the substitution of Mn for Co causes a decrease in electronic conductivity and electrocatalytic property. To lower the material cost without changing these two properties, substitution of Fe for Co, i.e. the use of LSCF (La₀⁶Sr₀⁴Co₀₂Fe₀₈O₃) as a cathode material, seems to be one of the best approaches for lowering the system cost. Figure 7 shows investment cost and system efficiency of SDC-system in which LSCF is used as a cathode. By using LSCF as a cathode, the system efficiency slightly decreases due to lower electrocatalytic activity of LSCF than that of SSC. On the other hand, the system investment cost slightly decreases by the substitution of LSCF for SSC. From the comparison of EC for both systems, the effect of substitution of LSCF for SSC turned out to be about 0.4 % cheaper EC. The EC can be further lowered by improvement of cathode microstructure suitable for a low overpotential. As an approach to further lowering of the system cost, substitution of lanthanum concentrate (crude grade) for a chemical grade La in LSCF is considered. We assumed that the cost of lanthanum concentrate is one-tenth of that of chemical grade La and electrical and electrochemical properties of cathode using lanthanum concentrate is the same with that of cathode using La with high purity. In that condition, by the substitution of lanthanum concentrate with La, the EC decreases by about 1.8 %.

Electricity Costs of Systems with Different Support Types. Another approach for the construction of cheaper system is to manufacture an anode-supported type tubular cell. It can not be applied for YSZ-system because low electronic conductivity of LSM causes very high ohmic loss at electrode with thinner thickness of cathode in an anode-supported type cell than that in a cathode-supported type cell. Therefore, we considered to construct a system using Ni-SDC, SDC, and LSCF as anode, electrolyte, and cathode materials respectively. The anode-supported type cell was assumed to be manufactured by the same process as cathode-supported type cell. Thicknesses of the anode, electrolyte, and cathode were first set as same as those of a typical cathode-supported type cell, i.e. 2, 0.02 and 0.1 mm respectively. The ECs for the system using the anode-supported type cell is shown in Fig. 8. The EC for the system using the cathode-supported type cell with the same cell component materials is also shown for reference. When the thickness of the
cathode is 0.1 mm, the sum of ohmic resistance at both electrodes is larger than that in the system using the cathode-supported type cell. The reason is that the electronic conductivity of LSCF is lower than that of Ni-cermet while the thickness of cathode is thinner than anode in the anode-supported type cell. Therefore, the system efficiency is lower than that of the system using cathode-supported type cell and resulted in more expensive EC. Next we changed the thickness of the cathode in order to lower the ohmic loss at the electrode. The EC for each system is also shown in Fig. 8. The EC decreases with increasing the thickness of cathode. By increasing the thickness of cathode up to 0.3 mm, the EC becomes lower than that of the system using the cathode-supported type cell. The anode material cost is large in the system using the anode-supported type cell. To lower that cost, increase of Ni ratio in cermet anode is effective because Ni is much cheaper than SDC. For example, by changing the Ni:SDC ratio from 4:6 to 8:2, the EC was lowered by about 1.4 %. The Ni:SDC ratio of 8:2 seems to be difficult at this moment from the viewpoint of the role of SDC particles in cermet anode to enlarge the triple phase boundaries, to match the thermal expansion, and to inhibit the sintering of Ni. However, there are possibilities to increase Ni fraction by the optimization of particle size distribution, usage of a low thermal expansion oxide and application of an anode with gradient structure.

**Electricity Costs of Systems with Two-Layered Electrolyte Structures.** As shown in Fig. 3, the influence of electronic conduction in reducing atmosphere on electromotive force is quite large in the SDC-system. To avoid the voltage drop by electronic conduction, electrolyte with a two-layered structure consisting of SDC and YSZ has been proposed by K. Eguchi (13). In order to evaluate the system in which a two-layered electrolyte is used, we have used assumptions as follows. YSZ layer with 5 µm thickness was deposited at the anode side of SDC layer with 15 µm thickness. The electronic conduction under reducing conditions was fully suppressed by the existence of YSZ layer. The electronic conduction at the interface of SDC and YSZ forming the Ce-Zr-O eutectic system was negligible. First we evaluated the system in which SSC/two-layered electrolyte/Ni-SDC are used as cell components. The EC for this system is shown in Fig. 9 as dotted line. The EC for the YSZ-system is also shown for reference. In the system using two-layered electrolyte, minimum EC is obtained at the current density of 0.7 A cm⁻². By the suppression of electronic conduction in reducing atmosphere, the terminal voltage of cell becomes as high as that obtained for the LSGM system as shown in Fig. 3 resulting in higher output power density. The application of two-layered
electrolyte turned out to be effective to lower the EC although extra manufacturing process is needed. Surface modification of YSZ with SDC at the cathode side is considered to have the same effect for the lowering of EC.

From the results obtained in the above evaluation, following conditions 1) ~5) were given for a new system to be evaluated. 1) The system is composed of LSCF/two-layered electrolyte/Ni-SDC as cell component materials. 2) An anode-supported type cell is adopted. 3) The thickness of cathode is 0.3 mm. 4) Lanthanum concentrate is used instead of La with high purity. 5) Ni:SDC ratio is 8:2.

The EC of this system is shown in Fig. 9 as a broken line. The minimum EC appears at the current density of 0.9 Acm⁻². By applying the improvements as described above at the same time, the EC of the system can be lowered by about 10% compared with that of the base YSZ-system.

CONCLUSIONS

Comprehensive evaluations of candidate materials for SOFC cell components were carried out for various systems using an SOFC/GT system as a platform for evaluation. The SOFC/GT system using YSZ as electrolyte were turned out to be economically feasible at the operation temperature of 800°C although further lowering of overpotentials are needed to achieve much lower system cost. Evaluations were carried out for several candidate materials for SOFC cell components and several approaches for lowering the system cost were also evaluated. Our results of evaluations indicate that by applying highly electronic conductive cathode and two-layered electrolyte to make a system more economical. Considerations of properties which are not considered in this manuscript and evaluations under various conditions should be done in a future work.

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