ABSTRACT

The progress and current status of research and development of planar SOFCs at Tokyo Gas are described. By coating the electrolyte with samaria-doped ceria (SDC) on the cathode side and doping YSZ in the Ni/YSZ anode with ceria, a high power density of 0.93 W/cm² was obtained in single-cells with self-supporting electrolytes. These modified electrode processing techniques have improved the long-term performance stability as well. A 3-cell stack with an internal-manifold design achieved a high power density of 0.41 W/cm², and was successfully operated at fuel utilization up to 80% with CH₄-H₂O fuels. A kW-class stack is to be assembled and tested to demonstrate the potential advantages of our stack design including high power density and direct internal reforming of methane. Some research works for reducing the operating temperature are also described.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have advantages such as a high electrical efficiency surpassing the conventional power generators, high-grade waste heat, and thereby a very high total efficiency. Furthermore, SOFCs can be assembled into a compact system because all the cell components are made of solids and fuel reformers can be eliminated by internally reforming the fuel within the cells. Among various types of SOFCs, planar SOFCs are expected to give high power densities and reduced manufacturing costs.

Tokyo Gas has been developing planar SOFCs for use as highly-efficient and compact on-site cogeneration systems since 1989. By continuously improving the single-cell performance and stacking technology, in 1993 we obtained a high power output of 1331 W with two stack modules, each having 47 self-supporting single-cells of 12 cm square [1]. However, the power density (0.14 W/cm²) and long-term performance stability of the kW-class stack were not sufficient. Then we have focused on increasing the power density and durability of single-cells and stacks as well as on verifying the viability of operation with internally reformed CH₄. Recently, efforts have been devoted also to
reduce the operation temperature; testing the single-cells with very thin self-supporting electrolytes and development of substrate-type cells have been started. This paper reports recent advances of research and development of planar SOFCs at Tokyo Gas.

SELF-SUPPORTING CELLS AND STACKS

Basic design

Figure 1 shows the basic design of our planar SOFC. The single-cells have a self-supporting tri-layered structure. The stack has an internal manifold configuration in which the single-cells and separators are alternately piled so that the perforations at the four corners of each single-cell and separator body can be connected to serve as inlet- and outlet-manifolds for fuel and air. The separator has grooves on both surfaces through which the fuel and air flow in opposite directions (counter-flow pattern). No sealing materials are used to avoid undesirable thermal stresses as a result of strictly bonding components with different thermal expansion characteristics. Sufficient gas sealing is achieved by arranging metal gaskets at the fringes of separators and applying a suitable load on the top of the cell-stack.

Materials and processing

The materials, thickness and manufacturing processes of the components are listed in Table 1. The electrolyte sheet is made of sintered 3 mol% Y₂O₃-stabilized zirconia (3YSZ) of 100 microns thick. On each surface of the electrolyte the cathode and anode materials are screen-printed and fired to form a single-cell. The temperatures for firing the cathode and anode are 1150°C and 1450°C, respectively. For the cathode, strontium-doped lanthanum manganite (LSM) is used. For the surface modification of the electrolyte, samaria-doped ceria (SDC) is screen-printed and fired before the cathode fabrication. The anode, typically Ni/8YSZ cermet, is prepared by the unique process called “pyrolysis of metallic soap slurry (PMSS)” [2]. This technique has been found to give highly-uniform dispersion of fine YSZ particles in the cermet, which avoids excessive sintering and grain growth of nickel particles and thereby significantly reduces the interfacial resistance. The PMSS technique has recently been modified to allow doping of ceria into 8YSZ in the cermet. The separator consists of three components: separator body and two current collectors. The body is made of alumina, which has a center opening, four perforations at the corners and grooves on the anode-side surface. A grooved plate of strontium- or magnesium-doped lanthanum chromite (LCM) is embedded in the separator body to serve as a current collector on the cathode side. A nickel mesh is used as a current collector on the anode side, which is electrically connected with LCM through the center opening in the body.
Single-cell performance

Figure 2 shows the V-I characteristics of three types of single-cells. The cells with a nominal size of 6 cm x 6 cm and an effective electrode area of 4 cm² were tested at 1000°C using hydrogen and air. The cell A having the Ni/YSZ PMSS anode and the LSM cathode gave a maximum power density of 0.57 W/cm². The cell B, whose cathode was modified by the SDC inter-layer, showed a higher maximum power density of 0.74 W/cm². Figure 3 shows the cross-sectional microstructural image of the cathode/electrolyte interface of the cell B. A dense and uniform SDC inter-layer of 2-3 microns thick is formed with good adherence to both the electrolyte and cathode. It was found from the half-cell tests that the dense SDC inter-layer greatly reduced the ohmic loss maybe associated with the contact resistance, while the polarization loss increased very slightly. In the cell C, whose anode was also modified by CeO₂-doping into 8YSZ in the cermet (denoted as Ni/(Ce)YSZ), the maximum power density further increased to 0.93 W/cm². It was considered that the increase of the number of electrochemically active sites in the vicinity of the anode/electrolyte interface resulted in the improvement of cell performance. The electronic conductivity of (Ce)YSZ was estimated to be high enough to expand the electrochemically active region near the interface.

The results of durability tests of single-cells with dry H₂ fuel are shown in Figure 4. The cell with the cathode modified by the SDC inter-layer (cell B) exhibited an improved durability as compared to the unmodified cell (A). It is to be noted that the degradation of the cell B after 1400 hours was almost negligible. Microstructural analyses after the durability tests showed that the cathode/electrolyte interface in the cell B remained intact while in the cell A reactions between 3YSZ and LSM had occurred which was accompanied by the coarsening of LSM grains near the interface. Thus the SDC inter-layer has been proved effective to improve both the initial performance and the long-term performance stability of single-cells.

Figure 5 shows the long-term performance of single-cells operated with H₂/H₂O and CH₄/H₂O (external reforming) fuels. The cell A showed a fast degradation occurred within 20 hours in H₂/H₂O fuel. The cell C, on the other hand, showed no initial performance drops both in H₂/H₂O and CH₄/H₂O fuels, and the degradation rate was reduced to 1.2 %/1000h. Under operation with practical fuels, the modifications of the cathode with the SDC inter-layer and of the anode with the ceria-doping not only increased the maximum power density but also improved the long-term performance stability.

Stack performance

Figure 6 shows the V-I and P-I characteristics of a 3-cell stack of 6 cm square single-cells. By using the cells with the modified electrodes and by optimizing structural details of the stack to have a better sealing efficiency, the internal resistance has been
greatly reduced, and the power density has increased up to 0.41 W/cm². The effects of fuel utilization and kind of fuels on the performance of a 3-cell-stack are plotted in Figure 7. For the CH₄/H₂O fuel, CH₄ was externally reformed before entering the cells. With a steam addition to the fuel, the cell voltage decreased due to an increase of oxygen partial pressure. In spite of this theoretical voltage decrease, the cell-stack was able to be operated at fuel utilization up to 80 % with both H₂/H₂O and CH₄/H₂O fuels. No distinct differences of cell voltage were observed irrespective of the kind of fuels.

Figure 8 shows the variation of cell voltage with the internal reforming ratio for a 3-cell stack of 12 cm square single-cells. The stack was tested at fixed current density (0.3 A/cm²) and fuel utilization (50 %). The cell voltage showed no changes over the whole internal reforming ratio ranging from 0 % (external reforming) to 100 % (direct internal reforming). This result promises an operation of the stack in the direct internal reforming (DIR) mode without causing any damages to the cell components due to the temperature differences induced by the endothermic reforming reaction. The potential advantages of the DIR SOFCs including higher efficiencies as well as compact and simplified system design are going to be demonstrated with an advanced kW-class stack that will be directly fueled by CH₄ and be operated at high fuel utilizations. The specification of the DIR stack now under assembly is given in Table 2.

CELLS FOR REDUCED TEMPERATURE OPERATION

A promising way to reduce the operation temperature of SOFCs is to lower the electrolyte resistance. Two ways of cell fabrication are possible for that purpose; the one is to reduce the electrolyte thickness and the other is to employ alternative electrolyte having higher ionic conductivity than the conventional electrolytes. We have started testing self-supporting single-cells with very thin 3YSZ electrolytes (~50 microns) and developing substrate-type SOFCs.

Figure 9 shows the V-I characteristics of self-supporting single-cells with very thin (50 microns) electrolytes. It is seen that the cells of this type give a sufficient power density (>0.35 W/cm² @ 0.7 V) at 900°C while at 800°C the performance falls to an unsatisfactory level (<0.2 W/cm² @ 0.7 V). Alternative modifications of microstructures and electrocatalytic activity of the electrodes are to be looked for.

The other approach we have been pursuing to reduce the electrolyte thickness is the development of substrate-type cells which have thin electrolyte films on porous electrode substrates. Two fabrication techniques have been tried to manufacture single-cells: the CVD-EVD and cofiring. Figure 10(A) shows the cross-sectional image of a substrate-type single-cell whose electrolyte was prepared by the CVD-EVD technique. A thin electrolyte film of 8YSZ was grown on a 5 cm x 5 cm porous substrate of Ni/YSZ.
cermet using vaporized chlorides of zirconium and yttrium [3]. A very dense and uniform film of about 20 microns thick was successfully grown with good reproducibility. The gas permeability was found to be as low as $1 \times 10^{-8}$ cm$^{-1}$g$^{-1}$s$^{-1}$, which ensures the gas tightness required for the electrolyte. The cathode was prepared by screen-printing of LSM on the electrolyte film and firing. The single-cell thus fabricated gave maximum power densities of 0.96 W/cm$^2$ at 1000°C and 0.61 W/cm$^2$ at 900°C, which has proved the possibility of operating the substrate-type cells at reduced temperatures.

For the fabrication of substrate-type cells at lower costs and with higher productivity, development of YSZ film-manufacturing technology by the cofiring has been started. A sol of YSZ fine particles was cast on the pre-sintered substrate of NiO/YSZ and simultaneously fired with the substrate. Typical microstructural image of the 8YSZ thin film prepared on a 6 cm x 6 cm substrate by the cofiring method is shown in Figure 10(B). The film of about 10 microns thick has been found to have a high density and good bonding to the anode substrate. The gas permeability of the cofired film was $8 \times 10^{-8}$ cm$^{-1}s^{-1}$, which is only slightly higher than that of the CVD-EVD film and will pose no problems for practical application as the electrolyte film. Preliminary results of testing this type of single-cells with platinum cathode showed a power density of 0.2 W/cm$^2$ at 800°C. By optimizing the material composition and microstructure of the electrodes, higher performance will surely be obtained at 800°C or lower temperatures.

FUTURE PROSPECTS

Since the development of the basic stack design in 1994 [4], we have focused on increasing the power density and fuel utilization rather than getting higher power outputs with larger cells and stacks. The single-cell performance has been greatly improved through carefully controlling the microstructure of the electrode/electrolyte interface. The structural details of the stack have been modified to achieve better mechanical integrity, which resulted in high power density of 0.41 W/cm$^2$ and operation at high fuel utilizations up to 80 % for 3-cell stacks of 6 cm square cells. The possibility of direct internal reforming has been experimentally demonstrated with 3-cell stacks of 12 cm square cells. Our next milestone will be manufacturing a kW-class stack with the direct internal reforming system and operating it using methane as a fuel. Highly efficient and reliable operation of the stack will be the most important concern. Concurrent efforts will be devoted to the development of substrate-type cells for lower temperature operations, which is aimed at reducing manufacturing costs and improving the long-term performance stability.
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![Diagram of Planar SOFC stack configuration.](image_url)

Figure 1 Planar SOFC stack configuration.
Table 1  Materials, thickness and manufacturing processes of SOFC components.

| Component | Material                | Thickness   | Manufacturing Process                  |
|-----------|-------------------------|-------------|----------------------------------------|
| Electrolyte | 3YSZ                   | 100 μm, 50 μm | Tape-casting & Sintering               |
| Cathode   | (La,Sr)MnO$_3$ (with SDC inter-layer) | 150 μm      | Screen-printing                        |
| Anode     | Ni / (Ce)YSZ           | 30 μm       | Screen-printing (modified PMSS*)       |
| Separator | Al$_2$O$_3$ / doped LaCrO$_3$ | 5 mm        | Pressing & Sintering                   |

* Pyrolysis of Metallic Soap Slurry [2]

Figure 2  Performance of single-cells.
Figure 3  Cross-sectional image of cathode/electrolyte interface with SDC inter-layer.

Figure 4  Durability of single-cells.

Figure 5  Durability of single-cells with H₂/H₂O and CH₄/H₂O fuels.
Figure 6  Performance of a 3-cell-stack.

Figure 7  Effects of fuel utilization and kind of fuels on the performance of a 3-cell-stack.

Figure 8  Variation of cell voltage with the internal reforming ratio for a 3-cell stack of 12 cm square cells.
Table 2  Specification of a kW-class DIR stack.

| Specification          | Value                  |
|------------------------|------------------------|
| number of single-cells | 50/stack x 2           |
| single-cell size       | 120 mm x 120 mm        |
| total electrode area   | 10000 cm²              |
| stack size             | 120 mm² x 220 mm² x 300 mm³ |
| operating temperature  | 1000°C                 |
| fuel                   | CH₄ (S/C=2)            |
| fuel utilization       | 70 %                   |
| air utilization        | 30 %                   |
| expected performance   | 0.2 W/cm² @ 0.3 A/cm²  |

Figure 9  V-I characteristics of self-supporting single-cells with thin (50 μm) 3YSZ electrolytes.

Figure 10  Cross-sectional images of (A) a substrate-type cell fabricated by CVD-EVD method and (B) YSZ film prepared on a NiO/YSZ substrate by the cofiring method.