DEVELOPMENT OF ANODE-SUPPORTED SOFC FOR REDUCED-TEMPERATURE OPERATION

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ABSTRACT

Low-cost manufacturing process for anode-supported SOFC suitable for reduced temperature operation has been developed. The single-cell manufactured by co-sintering of YSZ electrolyte and NiO/YSZ anode substrate showed a maximum power density of 0.67 W/cm² @ 1.38 A/cm² and rated power outputs of 0.48 W/cm² @ 0.7 V and 0.26 W/cm² @ 0.3 A/cm² at 750°C. The cell can be operated at high fuel utilization up to 80% giving d.c. energy conversion efficiency of 46.2% (LHV). The cell showed sufficient resistance to cathode poisoning by Cr-containing vapor coming from metallic components. Basic structural design of a cell-stack that is capable of mitigating thermal stresses and mechanically robust even in fast start-up and shut-down cycles has been completed, and preliminary tests are going on. Also given is brief description of manufacturing and testing of doped gallate cells for reduced temperature operation.

INTRODUCTION

Anode-supported SOFC having a thin YSZ electrolyte film can be operated at reduced temperatures, which offers advantages over the conventional SOFCs operating at around 1000°C such as mechanical robustness against fast thermal cycles and thermal stresses, lower materials and manufacturing costs, system compactness as a result of less heat insulation requirement, etc. The market opportunity for the SOFC systems using anode-supported cells can greatly be expanded, ranging from residential micro-cogeneration systems to small-scale distributed power generators and cogeneration systems for commercial and office buildings. These applications require operation capability for easy and frequent start-ups and shut-downs, which can be realized by the system based on the anode-supported SOFC, not by the conventional all-ceramic SOFC for high-temperature operation.

Tokyo Gas has long been involved in research and development of SOFC for high-temperature operation and has achieved important milestones including successful direct
internal reforming operation of a 1.7 kW planar stack (1), development of high-performance single-cell with maximum power density of 0.85 W/cm², rated power density of 0.52 W/cm² at 0.7 V and no voltage degradation over continuous operation of 1,500 hours (2), application of these high-performance cells to Sulzer HEXIS’s 1 kW system and its successful operation. To expand potential application area of SOFC, however, Tokyo Gas has quite recently concentrated its interests in research and development of anode-supported SOFC technology that will provide flexible system operation. The present paper reports our recent progress in the development of key technologies.

LOW-COST CELL MANUFACTURING PROCESS

Aiming at reducing cell manufacturing costs, we have employed the process of co-sintering of screen-printed YSZ paste on a compacted anode substrate which will be easily scaled-up for high-volume production. Adjusting the sintering shrinkage of the electrolyte layer by controlling the grain size distribution of the raw material powder to match the shrinkage characteristics of the anode substrate as well as optimizing the sintering schedule have greatly improved the yield of co-sintered cells. Figure 1 shows the microstructure of the single-cell which was manufactured by co-sintering of electrolyte-anode bilayer at 1500°C, and then by firing an interlayer of SDC (Ce₀.₈Sm₀.₂O₁.₉) and then a composite of LSCF (La₀.₆Sr₀.₄Co₀.₈Fe₀.₈O₃)/SDC as the cathode. It can be seen from the SEM image that a dense and uniform electrolyte layer with thickness of approximately 30 μm has successfully been obtained. As will be described later in detail, the reason for forming the SDC interlayer is to prevent cathode poisoning by Cr-compound vapor from metallic interconnectors. This kind of well-established ceramic processing without using novel technologies is expected to greatly reduce the cell manufacturing costs.

SINGLE-CELL PERFORMANCE

Basic Performance Characteristics

The single-cell has a nominal size of 50 mm by 50 mm with an effective electrode area (cathode area) of 4 cm² and anode thickness of 2 mm. Figure 2 compares the electrochemical performance of the single-cells with different cathode materials tested at 750°C using dry hydrogen as a fuel. It can be seen that the cell with LSCF-SDC cathode shows much better performance than the one with PSM (PrSrMnO₃)-SDC cathode: a maximum power density of 0.67 W/cm² @1.38 A/cm² and rated power outputs of 0.48 W/cm² @0.7 V and 0.26 W/cm² @0.3 A/cm². These power densities are comparable to or even higher than those regularly reported for self-supporting-type planar SOFC single-cells working at around 1000°C. Thus the performance of single-cell has been confirmed high enough to build a stack.
**Operation at High Fuel Utilization**

For the anode-supported SOFC, concentration polarization loss in the anode can be a crucial problem because fresh fuel (H₂ and CO) and electrochemical reaction products (H₂O and CO₂) have to diffuse through a thick anode substrate in the opposite direction between the flow field (fuel distribution channel) and the anode/electrolyte interface. Figure 3 shows dependence of cell voltage of the anode-supported single-cell at 750°C as compared with a self-supported cell at 950°C using humidified hydrogen (20 vol.% H₂O-H₂) as a fuel. The self-supported cell having a thin anode of approximately 20 μm thick can be virtually free of concentration polarization, and its voltage variation with fuel utilization falls on a theoretical prediction line. The voltage characteristics of the anode-supported single-cell shows the same behavior up to the fuel utilization of 80%, at which the d.c. energy conversion efficiency is 46.2% (LHV). Assuming that the same performance is obtained with CH₄, the d.c. efficiency is estimated to be as high as 55.7% (LHV), which is satisfactorily high for practical applications. At fuel utilizations of higher than 80%, the anode-supported cell has shown a steep voltage drop due to the mass transport limitation through the thick anode substrate. By reducing the thickness and increasing the porosity of the anode, the performance and efficiency will be further improved.

To study the effect of concentration polarization on the cell performance for the case of using a reformed fuel, a three-dimensional numerical model analysis was performed for a simplified single-unit model with bipolar gas channels with a counter-flow configuration (3). The results have shown that slower-diffusing CO significantly contributes to the concentration polarization especially in a binary gas system of CO-CO₂ but with the help of the shift reaction (CO + H₂O = CO₂ + H₂) hydrogen is generated instead of undesirable increase of CO concentration in a downstream of the fuel. Thus the concentration polarization loss can be suppressed to enable operation of cells at high fuel utilization.

**Demonstration of Mechanical Robustness**

Figure 4 shows a demonstration setup to prove simple configuration and mechanical robustness of the anode-supported single-cells. A single-cell bonded with an alloy support was heated rapidly by nearly direct exposure to a flame from a burner. The burner combusts methane at an air ratio of less than unity to supply both heat and partially oxidized fuel containing CO and H₂. Although a self-supported cell instantaneously cracks after burner ignition due to its poor thermal shock resistance, the anode-supported cell stably works to drive a motor fan in about five minutes and survives repeated demonstration experiments. Thus mechanical robustness of the anode-supported cell against thermal shocks and rapid thermal cycles has been experimentally verified.
STACK STRUCTURE

A basic stack structure for mitigating thermal stresses has been proposed as shown in Figure 5. The single-cell is bonded to a thin and flexible metallic support foil with a glass sealant or a brazing filler metal, which makes a single-cell unit. The single-cell unit is sandwiched by two metallic frames for internal manifolding. And an interconnector having a dimple structure is placed on the top. All components other than the single-cell are made of metallic alloy based on a ferritic stainless steel which has sufficient oxidation resistance under the cathode condition and a thermal expansion coefficient close to that of the single-cell. The contact resistance between the cathode and interconnector materials in air at 750°C was measured to be 23 mΩ cm², which is sufficiently low. Figure 6 shows two examples for performance test results of one-cell stacks. The stack #11 gives the maximum power density of 0.32 W/cm² (=0.6 A/cm² × 0.53 V) and the rated power density of 0.28 W/cm² (=0.4 A/cm² × 0.7 V). The stack #28 gives a better performance although the open circuit voltage is slightly lower than the expected value; the maximum power density of 0.38 W/cm² (=0.75 A/cm² × 0.51 V) and the rated power density of 0.28 W/cm² (=0.4 A/cm² × 0.71 V). Efforts to improve the stack performance focusing on reduction of contact resistance are in progress.

PREVENTION OF CATHODE POISONING BY Cr-CONTAINING VAPOR

The most commonly used cathode material based on Sr-doped LaMnO₃ (LSM) was found to quickly lose its electrochemical activity when used in contact with heat-resistant alloys containing chromium. The degradation of LSM cathode was found to be caused by transport of Cr-containing vapor generated from oxidation scale on the surface of the alloy to the electrochemical reaction sites and precipitation of Cr₂O₃ as a result of electrochemical reduction of the vapor (4). This kind of degradation of cathode is a crucial problem in using Cr-containing alloys and should be minimized.

For this purpose, most previous studies have focused on reduction of vapor pressure of the Cr-containing vaporous species by coating the alloy surface or by forming a vapor trap layer on the cathode (5-7). These remedies, however, may be limited in their life, so we have taken a different approach: to control the relative rate of electrochemical reductions of oxygen and Cr-containing vapor. The effect of the kinds of electrolyte and cathode materials on the degree of Cr-poisoning was studied (8). The results have shown that the degree of degradation of LSM cathode is very much dependent on the kind of electrolyte material; the electrochemical performance stability of LSM is much better on SDC (Ce₀.₇Sm₀.₃O₁.₉) and LSGM (La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃) than on YSZ and ScSZ. Then the best combination of cathode and electrolyte materials was identified as LSCF (La₀.₆Sr₀.₄Co₀.₈Fe₀.₂O₃)/SDC as shown in Figure 7. From these results, we see that the Cr-poisoning can be prevented by coating a SDC layer on the surface of YSZ electrolyte before firing LSCF cathode. Thus the critical problems of cathode degradation by poisonous Cr-containing vapor from the alloys have been fixed by a proprietary cathode/electrolyte interface modification technology.
DOPED GALLATE CELLS

Similarly to anode-supported cells, self-supported cells using higher oxide-ion conducting electrolytes such as doped lanthanum gallates can be operated at reduced temperatures. As one option to reduce operation temperature and looking into the possibility of direct electrochemical oxidation of hydrocarbon fuels (9), we also have conducted research work in the area of doped gallate cells. Although doped gallates give high oxide ionic conductivity, they show poor mechanical properties, so that we started with increasing the bending strength. By dispersing 2 wt% of Al$_2$O$_3$ grains into the matrix of La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.5}$, the three-point bending strength has successfully been increased from 120 MPa to 255 MPa at room temperature and from 80 MPa to 190 MPa at 800°C in air with no deleterious effects on ionic conductivity and thermal expansion coefficient (10).

Using a 200 μm thick sintered sheet of this dispersion strengthened material as the electrolyte, a single-cell with a nominal size of 60 mm by 60 mm was manufactured. The cathode is a composite of LSCF and SDC, while the anode is a composite of Ce-doped 8YSZ, SDC and Ni. Before firing these electrodes, SDC interlayers of 0.3 μm thick were formed on both surface of the electrolyte for the purpose of reduction of cathode polarization loss and preventing reactions between the anode and electrolyte. Figure 8 shows the electrochemical performance of a single-cell thus prepared as a function of operation temperature. The maximum power density at 650, 700, 750 and 800°C is 0.29, 0.46, 0.58 and 0.67 W/cm$^2$, respectively. Figure 9 shows the result of long-term performance test of single-cell at 750°C. The cell voltage continued to increase up to 0.9 V @0.3 A/cm$^2$ with no signs of degradation during the continuous operation of 1,000 hours. Thus, cells employing alumina dispersed doped gallate as the electrolyte can give good power output characteristics at reduced temperatures and long-term performance stability as well as increased mechanical strength.

SUMMARY AND FUTURE PLANS

Low-cost manufacturing process for anode-supported SOFC suitable for reduced temperature operation has been established. The single-cell manufactured by co-sintering of YSZ electrolyte and NiO/YSZ anode substrate showed a maximum power density of 0.67 W/cm$^2$ @1.38 A/cm$^2$ and rated power outputs of 0.48 W/cm$^2$ @0.7 V and 0.26 W/cm$^2$ @0.3 A/cm$^2$ at 750°C. The cell can be operated at high fuel utilization up to 80% giving d.c. energy conversion efficiency of 46.2% (LHV). Having achieved these satisfactorily high electrochemical performance in single-cells, we are going to place emphasis on the development of cell-stacks that are capable of mitigating thermal stresses and mechanically robust even in fast start-up and shutdown cycles.
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**Fig. 1.** Cross-section SEM image of the anode-supported cell manufactured by co-sintering of electrolyte and anode followed by cathode firing.

LSCF* / SDC**
SDC** (not visible in this picture)
8YSZ
Ni / YSZ substrate

*LSCF : (La, Sr)(Co, Fe)O₃
*SDC : Samaria Doped Ceria, Ce₀.₉Sm₀.₁O₁.₉

**Fig. 2.** V-I and P-I characteristics of anode-supported-type single-cells at 1023K.

**Fig. 3.** Fuel utilization rate dependence of cell voltage of anode-supported single-cell at 1023K as compared with self-supported cell at 1223K. The solid line shows a theoretical voltage calculated from the Nernst equation.
Fig. 4. Demonstration of simple configuration and mechanical robustness of anode-supported-type single-cells by rapid heating with a gas burner and electricity generation at reduced temperature.

Fig. 5. Structural design illustration of a stack using anode-supported-type single-cells and metallic component.

Fig. 6. Preliminary results of electrochemical performance tests of one-cell stacks using ferritic stainless steel components.
Fig. 7. Effect of electrolyte and cathode materials on the degree of Cr-poisoning, measured by using a cathode half-cell in contact with a plate of INCONEL 600.

Fig. 8. Performance of a self-supporting-type single cell at 923-1073K using 2 wt% Al₂O₃ dispersed La₉Sr₀₉Ga₀₈Mg₀₂O₂₈₅ as the electrolyte.

Fig. 9. Long-term stability at 1023K of a self-supporting-type single-cell, using 2 wt% Al₂O₃ dispersed La₉Sr₀₉Ga₀₈Mg₀₂O₂₈₅ as the electrolyte.