論 文 の 内 容 の 要 旨

論文題目　　A Novel Micro-tubular Solid Oxide Fuel Cell for Advanced Power Generation

（次世代発電システム用の新規マイクロ・チューブ型SOFCの開発）

氏　　名　　パンティ　ドゥルーバ

## 1. Introduction

In view of the problems related to current fossil-based energy systems such as the emission of greenhouse gases, resource depletion, and energy security, there has been an urgent need to move toward alternative energy sources and efficient energy utilization. Solid oxide fuel cells (SOFCs), which convert chemical energy in hydrocarbon fuels directly into electricity, are regarded as the next generation of energy conversion devices owing to their high efficiency and low environmental impact. Because SOFCs operate at a high temperature (typically 600–900 °C), their exhaust heat can be used for combined-cycle and cogeneration applications, thereby achieving significantly high system efficiencies. Among the different geometric designs of SOFCs, the micro-tubular design offers a number of advantages. A tubular configuration alleviates issues associated with high-temperature sealing between fuel and oxidant streams because the seals can be placed out of the high-temperature zones. Since the active surface area per unit volume is inversely proportional to the cell diameter, micro-tubular SOFCs possess a significantly high volumetric power density. Additionally, their smaller size also reduces the thermal gradients, thereby making micro-tubular SOFCs robust against thermal cycling. The present research aims to develop a novel type of micro-tubular SOFC using a facile and adaptable manufacturing method. The proposed micro-tubular SOFC design offers the advantages of improved current collection efficiency from the inner electrode as well as better performance under redox cycling conditions. Additionally, a conceptual study is presented for the integration of micro-tubular SOFC stacks with endothermic processes using a fluidized bed as the heat transfer medium.

## 2. Multi-step Dip Coating Method

Manufacturing is a key consideration for the performance, reliability, and cost-competitiveness of micro-tubular SOFCs. In the present research, a novel multi-step dip coating method was proposed, which offers several advantages such as simple control procedures, no high-cost equipment, and flexibility in terms of the size and thickness of the cell components. The method was applied to the fabrication of anode-supported micro-tubular solid oxide fuel cells (SOFCs) using carbon rods as combustible cores, as shown in Fig. 1. The fabricated micro-tubular SOFCs consisted of Ni-yttria-stabilized zirconia (YSZ), YSZ, strontium-doped lanthanum manganite (LSM)–YSZ, and LSM as the anode, electrolyte, cathode, and cathode current collector, respectively. Microstructural observations of the cell cross-section (Fig. 2) confirmed the homogeneity of different layers and their good adherence with each other. The micro-tubular SOFCs prepared for this study exhibited good electrochemical performance and they are competitive with the micro-tubular SOFCs fabricated by conventional processes such as extrusion. Because of the dominance of concentration

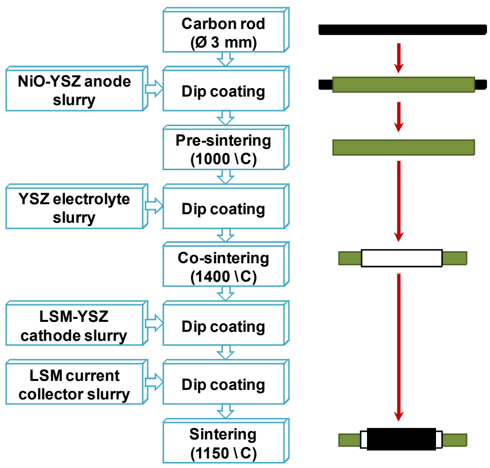


**Fig. 1** Schematic of the multi-step dip coating method

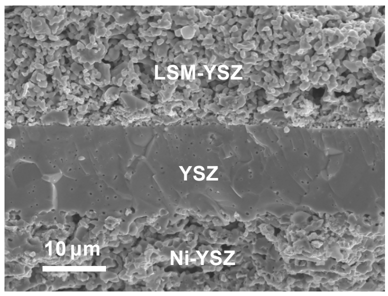


**Fig. 2** Cross-sectional SEM image of a tested micro-tubular SOFC

polarization on the anode side over that on the cathode side for the anode-supported designs, anode porosity was observed to play an important role in determining the overall cell performance. For the micro-tubular SOFC prepared without any pore former on the anode support, maximum power densities of 472, 402, and 333 mW cm$^{-2}$ were achieved at 850, 800, and 750 °C, respectively (Fig. 3a). These values increased to 582, 455, and 377 mW cm$^{-2}$, respectively, at 850, 800, and 750 °C as a result of the reduced anodic concentration polarization for the micro-tubular SOFC prepared using 10 wt% graphite pore former on the anode support (Fig. 3b).

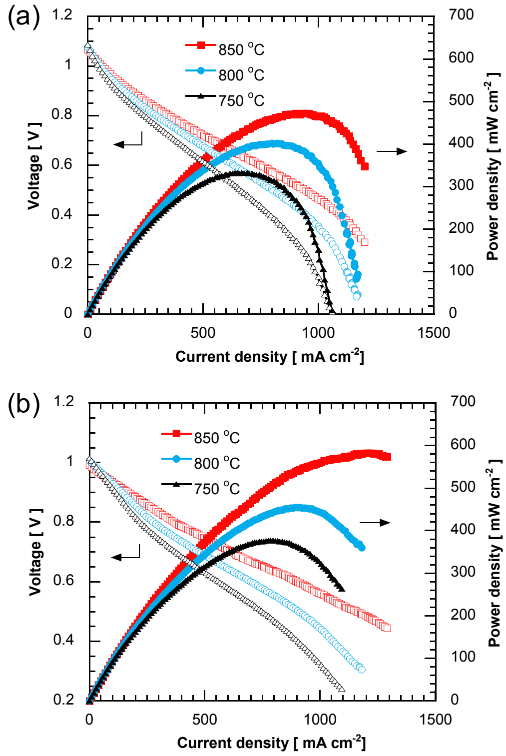


**Fig. 3** *I–V* curves for single cells: (a) with no pore former on anode support; (b) with 10 wt% graphite on anode support

### 3. Novel Micro-tubular SOFC with Inert Support

There is a significant ohmic resistance associated with current collection from the inner electrode (i.e., bore side) of existing micro-tubular SOFC designs. This ohmic resistance is proportional to the cell length. As a result, to keep the ohmic resistance to an acceptable level, the length of micro-tubular SOFCs developed so far has been in the range of only several centimeters. For developing large-scale SOFC systems, however, this limitation of the micro-tubular design needs to be overcome. Therefore, a novel micro-tubular SOFC design has been proposed, as shown in Fig. 4. This design consists of an inert ceramic layer to provide structural support to the cell. A thin current collecting layer is coated on top of the inert support so that current can be collected from the whole inner electrode surface, thereby minimizing the ohmic resistance. In addition to providing a better current collection efficiency, the proposed design also alleviates issues related to the performance degradation of anode-supported micro-tubular SOFCs under redox cycling conditions.

The thermal-fluid and electrochemical characteristics of the proposed micro-tubular SOFC design were studied through computational fluid dynamics (CFD) simulations. Owing to the significantly reduced ohmic resistance associated with current collection from the inner electrode, the proposed micro-tubular SOFC showed a much better *I–V* performance than the conventional anode-supported micro-tubular SOFC, as illustrated in Fig. 5. The simulation results suggested that for the optimization of the length of the proposed micro-tubular SOFC, the role of concentration losses should also be properly taken into account.

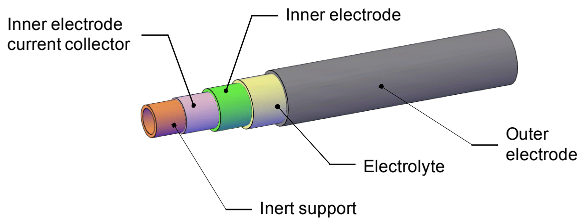


**Fig. 4** Schematic of proposed micro-tubular SOFC

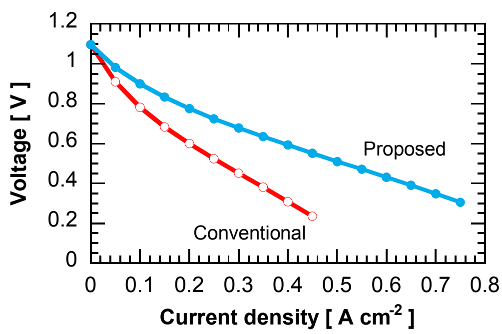


**Fig. 5** *I–V* curves for the proposed and conventional SOFCs (active length = 100 mm) at 850 °C

The proposed micro-tubular SOFC was successfully fabricated using the multi-step dip coating and co-sintering methods. Porous YSZ was selected as the inert support owing to the ready availability YSZ material as well as its proven compatibility with other SOFC component materials. The porosity of the YSZ support was maintained at 37% by adding micro-crystalline cellulose as a pore former and reducing the co-sintering temperature to 1300 °C. Fig. 6 shows a cross-sectional EDX image of the full cell after electrochemical testing. With humidified $H_2$ as the fuel and ambient air as the oxidant, the micro-tubular SOFC generated maximum power densities of 525, 442, and 354 mW cm−2 at 850, 800, and 750 °C, respectively (Fig. 7). These power densities are comparable to those of the conventional anode-supported micro-tubular SOFCs with similar component materials and active cell lengths. However, as suggested by the simulation study, the present micro-tubular design could be expected to deliver a distinctly better performance for longer cells with active lengths exceeding several centimeters.

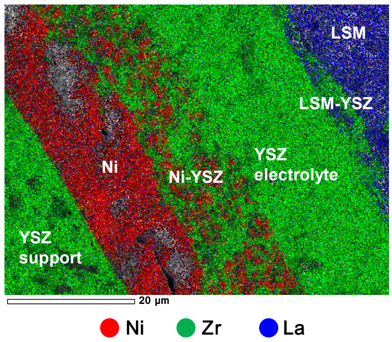


**Fig. 6** Cross-sectional EDX image of YSZ-supported cell showing different layers

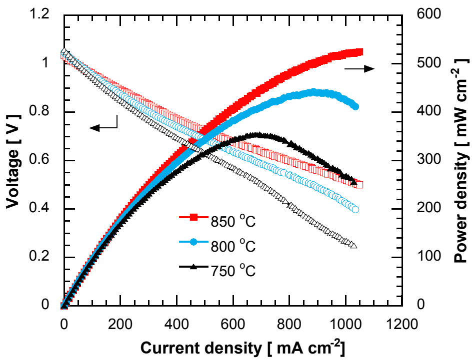


**Fig. 7** Power generation characteristics of YSZ-supported cell

## 4. Performance Improvement and Redox Cycling of Inert Support-based SOFC

The contribution of concentration polarization to the total cell resistance was found to be relatively high for the inert support-based micro-tubular SOFC. One of the possible approaches to reduce the concentration polarization is to optimize the microstructure of the inert support to enhance gaseous diffusion through it. To achieve this, a combination of micro-crystalline cellulose and polymethyl methacrylate (PMMA) pore formers was used. The micro-crystalline cellulose provides better shrinkage to the support layer at lower sintering temperatures, whereas the PMMA beads result in a macroporous structure with high porosity. In addition, this section aimed to study the effect of redox cycling on the inert support-based micro-tubular SOFC by alternately supplying humidified $H_2$ and air to the anode. The state-of-the-art Ni-YSZ anode may go through a number of alternate reduction and oxidation steps (redox cycles) during SOFC operating conditions, thereby causing significant local mechanical stresses in the anode as well as other cell components. However, compared to the conventional anode-supported designs, the mechanical stresses due to the redox cycling are expected to be considerably small for the present inert support-based micro-tubular SOFC, which consists of very thin layers of Ni current collector and Ni-YSZ anode.

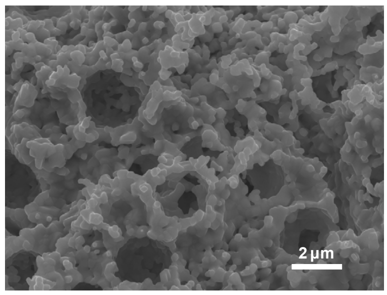


**Fig. 8** SEM image of YSZ support with macroporous structure

An SEM image of the YSZ support with macroporous structure is shown in Fig. 8. The porosity of the YSZ support was determined to be 43%. The single cell test showed that the maximum power densities of the cell were 616, 490, and 427 mW cm$^{-2}$ at 850, 800, and 750 °C, respectively. The improved cell performance was attributed mainly to the reduced concentration polarization resistance as a result of the enhanced gaseous diffusion through the YSZ support. Fig. 9 shows the effect of redox cycling on the cell voltage at a current density of 250 mA cm$^{-2}$. As

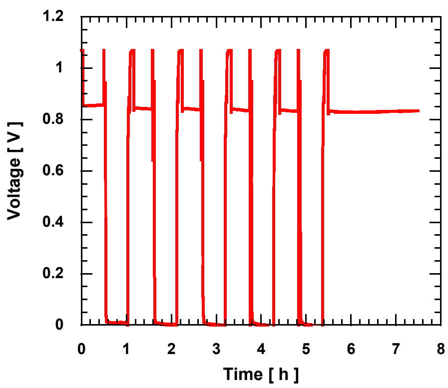


**Fig. 9** Variation of cell voltage with redox cycling at 250 mA cm$^{-2}$

can be observed, 97.3% of the initial performance was maintained after five redox cycles. In addition, there was no degradation in the OCV of the cell. Thus, the inert support-based micro-tubular SOFC showed an excellent tolerance toward redox cycling, which was attributable to the good adhesion between the cell layers and the accommodation of compressive stress developed during redox cycling by the formation of micro-cracks and microstructure coarsening.

**5. Integration of SOFC Stacks with Endothermic Processes**

The exothermic heat from SOFC stacks can efficiently be utilized by integrating them with endothermic processes such as gasification of coal and biomass, and steam reforming of natural gas and liquid hydrocarbon fuels. However, for the practical implementation such integrated systems, the high-temperature heat exchange is a crucial issue. In the present study, a fluidized bed was proposed for transferring high-temperature heat from SOFC stacks to the endothermic reactors. Because of its excellent thermal transport properties, the fluidized bed could offer a high rate of heat transfer from SOFC stacks and avoid such issues as the formation of "hot spots" due to non-uniform heat transfer. To elucidate the heat transfer behavior of SOFC stacks in the proposed integration, CFD simulations were performed considering a bundle type micro-tubular SOFC stack with a carbon steel enclosure. Fig. 10 shows temperature distribution in a SOFC stack comprising 30 micro-tubes, immersed in the fluidized bed. A maximum temperature difference of 131 K was observed in the stack, which can be considered to be within an acceptable range. The temperature distribution in the SOFC stack was found to be influenced by the design parameters such as fuel flow rate, cell length, and stack diameter and pitch between the SOFC micro-tubes.

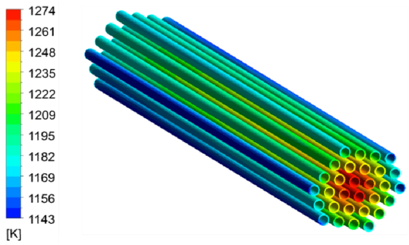


**Fig. 10** Temperature distribution in SOFC stack

**6. Conclusions**

Micro-tubular SOFCs are promising energy conversion devices, which offer several advantages over competing SOFCs such as high volumetric power density, good endurance against thermal cycling, and flexible sealing between fuel and oxidant streams. The present work was focused on the development of a micro-tubular SOFC with improved current collection efficiency and high operational stability for advanced power generation applications. The main achievements of the present work can be summarized as follows.

- A novel multi-step dip coating method was developed and successfully applied to the fabrication of anode-supported micro-tubular SOFCs. The anode porosity was found to play an important role in improving the overall performance of the micro-tubular SOFC by reducing the concentration polarization.
- A novel micro-tubular SOFC design with an inert support and a dedicated current collector layer for the inner electrode was proposed to achieve high current collection efficiency along with stable performance under redox conditions. The proposed design was realized using the multi-step dip coating and co-sintering methods, in which porous YSZ served as the inert support.
- The performance of the inert support-based micro-tubular SOFC was improved by optimizing the porosity of the porous YSZ support. Redox cycling of the cell showed an excellent tolerance toward the redox phenomenon with 97.3% of the initial performance maintained after five redox cycles.
- A conceptual study was presented for the integration of micro-tubular SOFC stacks with endothermic processes using a fluidized bed as the heat transfer medium. CFD simulations showed that with careful design considerations, it was possible to maintain the maximum temperature difference in the SOFC stack within an acceptable range and the fluidized bed was found to be effective for the thermal management of SOFC units.