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STACK PERFORMANCE OF INTERMEDIATE TEMPERATURE-OPERATING SOLID OXIDE FUEL CELLS USING STAINLESS STEEL INTERCONNECTS AND ANODE-SUPPORTED SINGLE CELLS

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ABSTRACT

We are continuing a national project to develop 1 kW-class SOFC system for Residential Power Generation (RPG) application supported by Korean Government. For intermediate temperature operation, we chose anode-supported, planar type SOFC design to have advantages for commercialization of SOFCs considering mass production and using cost-effective interconnects such as ferritic stainless steels. Anode-supported single cells with thin electrolyte layer of YSZ or ScSZ, respectively, were fabricated and their small stacks were built and evaluated. The size of anode-supported single cells finally sintered was about 10 x 10 cm², and the thickness of electrolyte and the cathode layer was about 20μm and 30μm, respectively. The I-V and AC impedance characteristics of these single cells and small stacks were evaluated at intermediate temperature (650 ~ 800 °C) by using hydrogen gas as a fuel. We have already carried out long-term performance test for YSZ thin electrolyte single cell for above 33,000 h (3.8 years) at 750 °C, applying 0.76 V with power density of 200 mW/cm². Using these YSZ thin electrolyte 10 x 10 cm² cells and Inconel interconnect plates coated by silver paste, the 15-cell and 60-cell short stack were prepared. The initial stack voltage at 150 mW/cm² was 12.5 V in hydrogen as fuel of 120 sccm/cell at 750 °C and decreased to about 10.9 V at 500 h operation time. It was then stabilized until 4,000 h with a degradation rate of 10 mV/(1000h, 1 cell). AC impedance of this small stack and microstructure of cell components were analyzed during and after the operation. Furthermore ScSZ thin electrolyte 10 x 10 cm² cells and ferritic stainless steel interconnects were built into a 5-cell stack and the small stack was operated at 650 °C for cost-effective planar SOFC RPG system. I-V and AC impedance characteristics of the small stack were evaluated at 650 °C by using hydrogen gas or methane gas as fuel.

Keywords: solid oxide fuel cell, SOFC, residential power generation, natural gases

1. INTRODUCTION

Solid oxide fuel cell (SOFC) is considered as important technology for residential power generation (RPG) applications to solve national energy problems in Korea. We have recently started a national project to develop 1 kW-scale SOFC system for residential application using liquefied natural gas (LNG) infrastructures supported by Korean government. Our main focus for this project is to develop intermediate temperature-operating SOFC system to be able to use metallic interconnects such as ferritic stainless steels. Lower operating temperatures enable us to use low cost interconnects, housing materials and other BOP (balance-of-plant). To obtain lower operating temperatures without significant compromise of cell performance, anode supported planar-type design with thin electrolyte structure was chosen.

Fabrication process of planar-type SOFC cells in our laboratory is quite mature to make 5 x 5 cm² and even 10 x 10 cm² with low cost and reasonable quality control. As seen in another paper of this proceeding written by us, we have reported long term performance for 26,000 hours (3 years) on 5 x 5 cm² single cell without significant degradations.

Before using stainless steel interconnects, we investigated single cell performance extensively and have built 15-cell and 60-cell stacks by using Inconel as interconnects. From those experiences 4-cell stack with ferritic stainless steel as interconnects were fabricated and tested.

In this paper, we like to report and discuss about SOFC performances of single cells and stacks in further detail.



(a) 15-cell stack (b) 60-cell stack

Fig. 1. Photographs of 15-cell and 60-cell stack using Inconel as interconnects

2. EXPERIMENTS

2-1. Single Cell Fabrication

2-1-1. Single cell for higher temp. operation (750°C)

Anode-supported single cells with thin YSZ electrolyte were fabricated by following processes. Mixture of NiO and YSZ (8 mole% Y_2O_3 -ZrO₂, 8YSZ) powders with weight ratio of 5:5 were prepared by ball-milling process. Then 24 vol% of graphite powder as a pore-former and organic binder(PVB) were added in the powder mixture using ethyl alcohol as a solvent. After milling and drying, the mixture was pressed into the form of anode plate and pre-sintered at 1400°C for an hour. The size of anode substrate was about $6 \times 6 \text{ cm}^2$, with a thickness of $\sim 2 \text{ mm}$. Thereafter 8YSZ slurry was coated on the substrate by dipping and the substrate was sintered at 1550°C for 2 hours to make a fully dense electrolyte layer with thickness of about 20 μm . The size of the cell was reduced after sintering into $5 \times 5 \text{ cm}^2$ and the thickness of the cell was about 1.8 mm. On the surface of the electrolyte (8YSZ) layer, the paste of LSM ($La_{0.7}Sr_{0.2}MnO_3$) and 8YSZ with a weight ratio of 5:5 was printed and heat-treated at 1100°C for 2 hours, thus finally an anode-supported single cell of SOFC was produced with active cathode area of $4.5 \times 4.5 \text{ cm}^2$.

2-1-2. Single cell for intermediate temp. operation (650°C)

Similar procedure was used to make anode-supported cell except using a functional layer on anode side with same NiO-YSZ composition and different porosity to ensure lower anode polarization. The functional layer of anode was introduced by screen printing technique on the surface of anode plate. 8YSZ layer was deposited by the same way as upper case on the top of the anode.

For lower operating temperatures (500 \sim 700°C) $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_{3-d}$ (LSCF) was used as cathode material. LSCF was mixed with Sm-doped cerium oxide ($Ce_{0.8}Sm_{0.2}O_{2-d}$, CSO) with weight ratio of 5:5. The LSCF-CSO paste was coated on YSZ electrolyte layer and followed by heat treatment at 1100°C for 2 hours. Thin CSO layer (thickness $\sim 2 \mu\text{m}$) was deposited on YSZ electrolyte to inhibit undesired reaction between the cathode and the electrolyte

2-2. Stack Preparation

2-2-1. Stack using Inconel as interconnects for high temperature operation (750°C)



Fig. 2. Photograph of 4-cell stack using STS 430 as interconnects

15-cell and 60-cell stacks were built by using Inconel as interconnects as seen in Fig. 1. A 15-cell SOFC module was fabricated by stacking in series and a 60 cell module was stacked by 2 x 2 array configuration using the same $5 \times 5 \text{ cm}^2$ cells.

Low temperature-melting borosilicate was used for sealing of stack. Internal manifold design was introduced and cross-flow type channel was manufactured at the Inconel interconnects. To prohibit undesired oxidation at the cathode side of interconnects, silver paste was coated on interconnects surface. Inconel mesh was introduced for better electrical contact and current collection between interconnects and cells for cathode side. Inconel mesh was also coated with LSM-silver paste to prevent undesired oxidation. Ni felt was introduced for the same purpose at the anode side. Measurement and monitoring were carried out for each layer of the stack at 15-cell stack.

2-2-2. Stack using Stainless Steel as interconnects for intermediate temperature operation (650°C)

A 4-cell stack module was built for intermediate temperature operation by introducing stainless steel (STS 430) as interconnects as seen in Fig. 2.

STS 430 has several merits as interconnects material relative to Inconel such as lower cost and easier manufacturing processes. However, our past experiences reveal that STS 430 shows low oxidation durability even at 650°C, especially for cathode side. To overcome this problem, composite paste of LSM and silver was fabricated and coated at the side of cathode of STS 430 interconnects. Inconel mesh coated with silver paste and Ni felt were introduced for better current collection by the same manner as mentioned earlier. Each layer was separately measured by frequency resonance analyzer and dc measurement facilities to monitor cell behaviors.

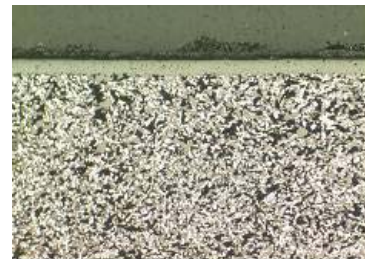


Fig. 3. Microstructure of anode-supported SOFC

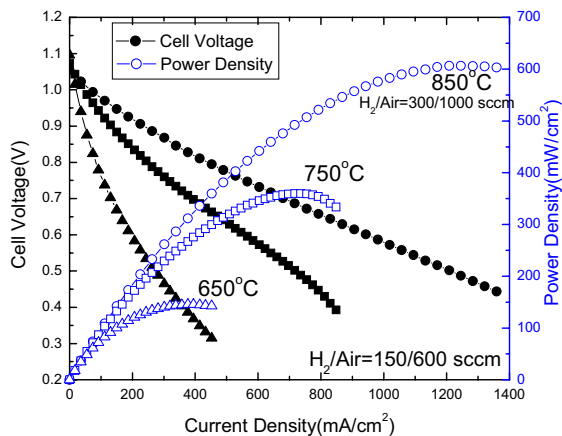


Fig. 4. Single cell performance of 5 x 5 cm² (LSM/YSZ/Ni-YSZ)

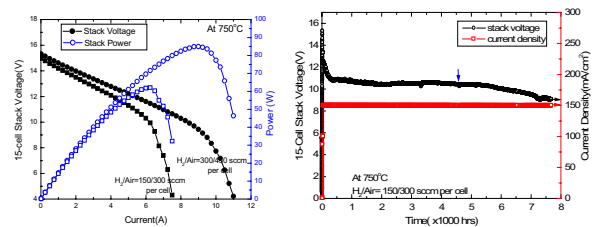
3. RESULTS AND DISCUSSIONS

Figure 3 shows a typical microstructure of our cell. The thickness of YSZ electrolyte was about 20 μm and dense enough to ensure gas tightness. The average porosity of anode area (after reduction) was measured as about 24 % by mercury porosimetry technique.

Our cell showed quite stable performance over extensive time period of about 3 years.

5 x 5 cm² single cell performance was measured by using neat hydrogen with 3 % of humidity as a fuel and air as an oxidant as seen in Fig. 4. Flow rates of hydrogen and air were 150 and 600 sccm (standard cubic centimeter per minute) at temperature range of 650 ~ 750°C, respectively. The flow rates were increased to 300 sccm for hydrogen and 1000 sccm for air because concentration overpotential behavior was observed at high current density region. At 850°C the cell showed as high as 600 mW/cm² of power density.

A 15-cell stack was built by using the 5 x 5 cm² cells as seen in Fig. 1. Performance of the stack is shown in Fig. 5(a). The stack shows power output of 60 W at lower gas flow rates. The stack exhibits significant concentration overpotential problem and the current range of concentration overpotential was increased by higher flow rate of gases as seen in Fig. 5(a). This problem will be mentioned again by showing each cell voltage later. The long-term stack performance was monitored as seen in Fig. 5(b). Current density was kept as constant and stack voltage was measured. The stack performance was sharply decreased at first 300 hours and stabilized after the period. The initial degradation of the stack may be mainly due to oxidation of interconnects at cathode sides. Each layer of cell performance was monitored as seen in Fig. 6. Current density value “0” means open circuit situation. In this condition 15 cells show very uniform open circuit voltages as seen in Fig. 6. However, when current of stack was increased, each cell voltage was not uniform any more. Especially, cell voltages show substantial differences at the highest current situation.



(a) I-V Characteristics (b) long-term data

Fig. 5. Performance of 15-cell stack at 750°C

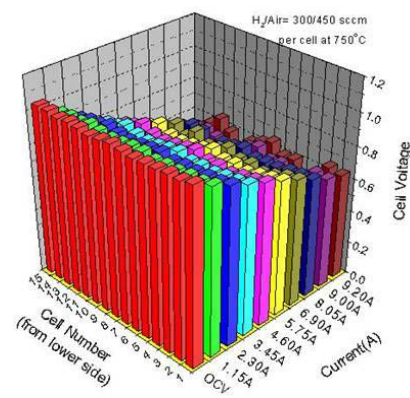


Fig. 6. Each cell performance at 15-cell stack

This means that gas distribution at each cell is not uniform and makes concentration overpotential problem. This requires further improvement at stack design and configurations. The 60-cell stack built by 2 x 2 cell array configuration was also successfully operated for about 500 hours. However, the performance was sharply degraded after the initial period mainly due to oxidation of metal interconnects and operation was terminated. This problem motivated us to decrease operating temperature and LSCF and stainless steel were considered as cathode and interconnects system. To achieve intermediate temperature performances, LSCF-CSO composite cathode was introduced and the cell characteristics were measured as seen in Fig. 7. Thin functional layer (thickness ~ 15 μm) for anode to enhance cell performance also deposited on YSZ electrolyte. Single cell performance was greatly enhanced compared to the traditional LSM/YSZ/Ni-YSZ sample as seen Fig. 7(a) at the same temperature. Figure 7(c) shows ac impedance response for two cells at 750°C. LSCF sample shows improved IR behavior (left-hand intercept at Re Z axis) compared to LSM sample. This may be due to the functional layer effect at anode side and improved cathode performance. LSCF sample shows about 400 mW/cm² of maximum power density even at 650°C of cell temperature as seen in Fig. 7(b) and the impedance response difference between LSCF and LSM becomes bigger than at 750°C.

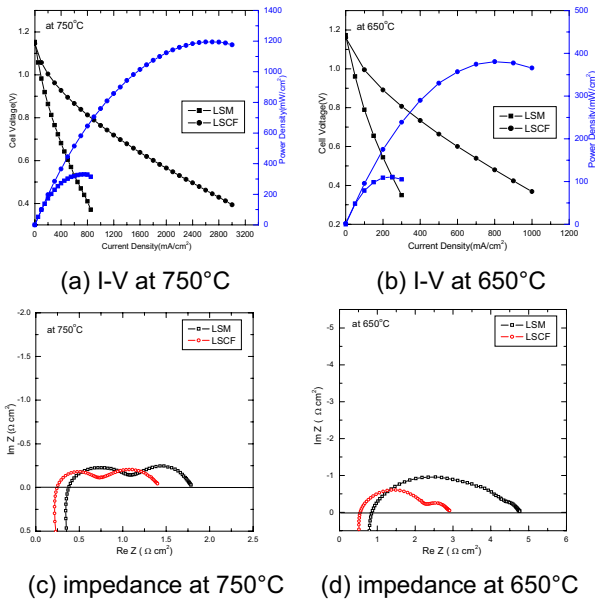


Fig. 7. Single cell performance comparison for LSM and LSCF samples

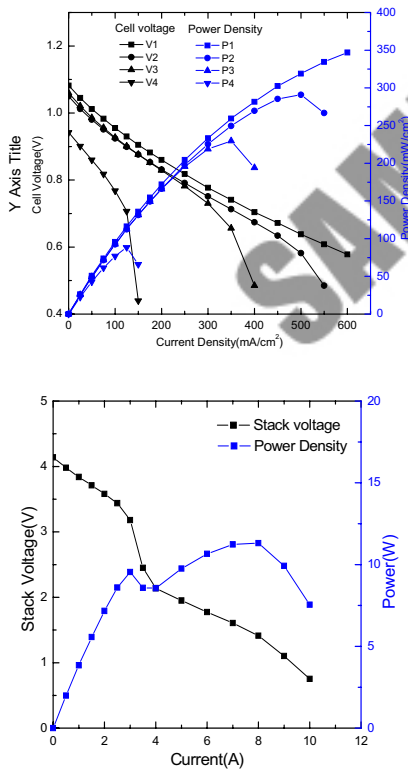


Fig. 8. Performance of 4-cell stack at 650°C (LSCF and STS 430 were used as cathode and interconnects)

A 4-cell stack was built by using LSM/silver coated STS 430 interconnects. Stack performance is shown in Fig. 8(a). This graph shows sharp voltage drop at about 3 A of current and drop of power. This is mainly due to non-uniform performance of each cell as seen in Fig. 8(b).

Cell number 1 is placed at the gas inlet region and cell number 4 is at the end of stack and therefore deficient gas flow at the cell number 4 makes very low power output. Furthermore, we found some parts of sealant material were blocking gas path at the manifold of cell number 4 from investigations after stack operations. However, non-uniformity was found to be very important issue to deteriorate stack performances even at small stack like 4-cell arrangement. More advanced approach for stack design and construction such as manifold, pressure drop and flow paths are required.

4. CONCLUSIONS

1. Single cell performance using LSM as cathode material was measured at temperature range of 650–850°C. A 15-cell and a 60-cell stack were constructed based on the single cell performance and by using Inconel as interconnects material. The 15-cell stack showed stable performance over 8000 hour period at 750°C. Sharp performance degradation at initial state is considered to be mainly due to oxidation of interconnects.

2. Single cell using LSCF as cathode showed great performance at intermediate temperature range. On the bases of investigations for the single cell, a 4-cell stack was built by using STS 430 as interconnects to operate at 650°C. The result shows great possibility of intermediate temperature operation of SOFC by using stainless steel and LSCF as interconnects and cathode material on YSZ electrolyte, respectively.

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