PERFORMANCE OF SINGLE CELLS AND SHORT STACKS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL USING THIN ELECTROLYTE OF YSZ AND ScSZ

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ABSTRACT

We have launched a project to develop a 1-kW-class SOFC system for residential power generation (RPG). Using cost-effective interconnects such as ferritic stainless steel, we developed an anode-supported, planar-type 1.2-kW-class SOFC stack that can be operated at intermediate temperatures (650° or 700°C). To achieve better cell performance at reduced temperatures, we improved cathode performance by replacing LSM with LSCF, a mixed conducting material. Then we introduced the functional layered structural concept at the anode substrate. Finally, we used ScSZ (scandia stabilized zirconia) instead of YSZ (yttria stabilized zirconia) for a thin electrolyte, about 20 μm thick. Anode-supported single cells were manufactured by press molding, screen printing technology, and a cofiring process, then formed into 5 x 5 and 10 x 10 cm² cells about 1.8 mm thick. We evaluated the I-V and AC impedance characteristics of improved single cells and long-term performance of small stacks at intermediate temperatures using hydrogen gas as fuel.

INTRODUCTION

The main focus of our research is developing an intermediate-temperature operating solid oxide fuel cell (SOFC) system using metallic interconnects such as ferritic stainless steel. Lower operating temperatures enable us to use low-cost interconnects, housing materials, and other balance of plant (BOP). However, operating SOFCs at lower temperatures makes cell performance less efficient due to deactivation of electrochemical reactions in the electrode and higher internal resistance of the electrolyte and/or single cell. To obtain lower operating temperatures without significantly compromising cell performance, an anode-supported, planar-type design with thin electrolyte structure was chosen, and alternative electrode and electrolyte materials were investigated (1,2).

The fabrication of planar-type SOFC cells in our laboratory is mature enough to produce 5 x 5 and even 10 x 10 cm² cells at low cost with reasonable quality control. In previous work, we obtained long-term performance (26,000 hr or over 3 yr) on 5 x 5 cm² single cells without significant degradation. Before using stainless steel interconnects, we investigated single-cell performance extensively and built 15- and 60-cell stacks using...
Inconel interconnects. From those experiences, 5-cell stacks using ferritic stainless steel interconnects were fabricated and tested with 5 x 5 and even 10 x 10 cm² cells. In this paper, we discuss the performance of SOFC single cells and stacks in further detail.

EXPERIMENTS

Fabrication of Single Cells

We synthesized the raw materials of a cathode, LSM (La₀.₇Sr₀.₃MnO₃) or LSCF [(La₀.₆Sr₀.₄)(Co₀.₂Fe₀.₈)O₃] by the citrate method (4). The LSM and LSCF powders were calcined at 800°C for 1 hr and at 1000°C for 8 hr, respectively. X-ray diffraction patterns were analyzed to confirm single perovskite phases of LSM and LSCF. Each anode-supported single cell with composite cathode [LSM+YSZ(ZrO₂+8Y₂O₃, 8YSZ)] or [LSCF+CSO (Sm-doped cerium oxide, Ce₀.₈Sm₀.₂O₂₋₁₋₄)] was prepared on top of the fired YSZ thin electrolyte surface. For anode substrates, nickel oxide and yttria-stabilized zirconia powders (ZrO₂+8Y₂O₃, YSZ) were primarily mixed and milled together at a weight ratio of 50:50 in a powder mixture. Then 24 vol% graphite powder as a pore-former and organic binder were mixed into the powder mixture with ethyl alcohol, and the mixture was dried in an oven. The NiO+YSZ powder mixture was pressed by a rectangular mold and pre-sintered at 1400°C for 1 hr to prepare the anode substrate. The size of this porous anode substrate was about 6 x 6 cm² and 2 mm thick. Thereafter, the YSZ (8 mol% Y₂O₃+ ZrO₂) or ScSZ (10 mol% Sc₂O₃+1 mol% CeO₂+ ZrO₂) electrolytes were slurry coated on the substrate and sintered at 1550°C for 2 hr to form a dense electrolyte layer with a thickness of about 20 μm. Cell size was reduced to 5 x 5 cm² after sintering, and the cell substrate was about 1.8 mm thick. On the surface of the electrolyte (YSZ or ScSZ) layer, the composite cathode mixtures of (LSM+YSZ) or (LSCF+CSO) with a weight ratio of 50:50, respectively, were printed with a thickness of 30 μm and heat-treated at 1100°C for 2 hr. The final products of anode-supported single cells with activate cathode area of 4.7 x 4.7 or 9.7 x 9.7 cm² are shown in Figure 1.

Figure 1. Photograph of anode-supported single SOFCs (5 x 5 and 10 x 10 cm²).

Preparation of Short Stacks

First, 15- and 60-cell stacks were built using Inconel as interconnects, as seen in Figure 2 (5). A 15-cell SOFC module was fabricated by stacking in series, and a 60 cell module was stacked in a 2 x 2 array using the same 5 x 5 cm² cells seen in Figure 2 (b).
Low temperature-melting borosilicate glasses were used for sealing the stack. Internal manifold design was introduced, and a 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 the interconnect surfaces. Inconel mesh was introduced for better electrical contact and current collection between interconnects and cells for the cathode side. Inconel mesh was also coated with silver-LSM paste to prevent undesired oxidation. Ni felt was inserted for the same purpose at the anode side. Each layer of the 15-cell stack was measured and monitored.

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

Figure 2. Photographs of 15- and 60-cell stacks using Inconel as interconnects.

Second, a 5-cell stack module was built for reduced temperature (650°C) operation by introducing stainless steel (STS 430) as interconnects, as seen in Figure 7. STS 430 has several merits as interconnect material relative to Inconel, such as lower cost and easier manufacturing. However, past experience reveals that STS 430 shows low oxidation durability even at 650°C, especially for the cathode side. To overcome this problem, a composite paste of LSM and silver was fabricated and coated on the cathode side of STS 430 interconnects. Inconel mesh coated with silver-LSM paste and Ni felt were introduced for better current collection by the same manner mentioned earlier. Each layer was measured separately by frequency resonance analyzer and DC measurement facilities to monitor cell behaviors.

RESULTS AND DISCUSSION

LSM/YSZ/(Ni-YSZ) Cells and Stacks

A 15-cell stack was built using the 5 x 5 cm² cells seen in Figure 2. Stack performance is shown in Figure 3(a). The stack shows power output of 60 W at lower gas flow rates and exhibits a significant concentration overpotential problem. The current range of concentration overpotential was shifted to higher values by a higher flow rate of gases, as seen in Figure 3(a). Long-term stack performance was monitored (Figure 3 b). Current density was constant and stack voltage measured. Stack performance decreased sharply during the first 300 hr and stabilized after that. This initial degradation may be due mainly to oxidation of interconnects (Inconel 600) at cathode sides. Each layer of cell performance was monitored. In open circuit condition, 15 cells show very uniform OCV (open circuit voltages). However, when the stack current was increased, cell voltage was no longer uniform and substantial differences exist at the highest current.
In this stack we used an anode-supported LSM/YSZ/Ni-YSZ system. When hydrogen was used as fuel, the cells in individual performance tests showed maximum power density of 0.33 W/cm² at 750°C and 0.11 W/cm² at 650°C, as shown in Figure 6. Then, the single cell shows a resistance of 0.34 ohm cm² at 750°C and 0.75 ohm cm² at 650°C from the analysis of AC impedance responses. When AC impedance responses of the cell at OCV are measured, IR loss (Rₒ) can be read from the left-hand intercept (high-frequency region) of the X-axis of the response, and resistance value from the arc represents an electrode overpotential. The AC impedance arc can be separated by two or three semicircles that are considered related to the polarization arising from gas phase diffusion and electrodes. Although the cell showed relatively high resistance from AC impedance analysis, it exhibited excellent performance for long-term stability, as seen in Figure 4. For the long-term stability test, 0.2 A/cm² of current was applied, and voltage was monitored continuously.

![Figure 3. Performance of 15-cell stack at 750°C.](image)

![Figure 4. Long-term performance of anode-supported single cell using hydrogen as fuel at 750°C.](image)

The cell in Figure 4 exhibited only 7 mV/1000 hr (less than 1%) of degradation over 26,000 hr (3 yr). There was a furnace failure after 12,000 hr so the cell cooled completely to room temperature; then measurement resumed after furnace repair. By
5000 hr after the failure, cell performance had recovered to 85% of its original value, though there was unrecoverable damage of contact at the cell holder from the failure. Assuming no experimental failure, the degradation ratio can be as low as 0.5%/1000 hr. Anode-supported SOFCs were expected to have a worse degradation rate due to the thin electrolyte structure. However, our long-term performance relieves the concern and enables us to expect far longer stable performance when operating temperature is lowered.

As shown in Figure 3 (b), the serious performance degradation of the 15-cell stack after about 6000 hr seems to result not from cell degradation but from oxidation of metallic interconnects (Inconel 600) in the cathode side at 750°C. Also we assume that gas distribution at each cell is not uniform due to the sealing method, which creates a concentration overpotential problem that requires further improvement in stack design and configuration. The 200-W class stack using 60 cells built by 2 x 2 cell array, shown in Figure 2 (b), was successfully operated for about 500 hr, but 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 interconnect system.

**LSCF/YSZ/Functional-Layered (Ni-YSZ) Cells and Stacks**

One of our main research interests for SOFC is using cost-effective stainless steel for interconnects by lowering operating temperature. Ferritic stainless steel such as STS 430 has a thermal expansion coefficient (TEC) of 10.5 x 10⁻⁶°C, which is relatively close to that of YSZ. One of the main technical issues to lowering operating temperatures for SOFCs is high cathode resistance. To overcome this problem at intermediate temperatures (600°C ~ 700°C), LSCF replaced LSM cathodes (3,4). Although Ni-YSZ cermet shows reasonable performance at intermediate temperatures, the microstructure of the anode was modified to ensure better cell performance by applying a multilayer concept.

A thin and relatively dense functional layer (FL) of anode was fabricated between YSZ and the supportive anode plate to improve the anode activity, as shown in Figure 5 (a). The FL was about 15 μm thick and the pore size about 1 μm, which is smaller than the average pore size of ~ 5 μm for supportive anode areas. The performance of this cell is shown in Figure 6. Maximum power density was enhanced to 1.2 W/cm² at 750°C.

![Figure 5. Microstructures (cross-section) of improved anode-supported single cell with YSZ and ScSZ electrolyte and 0.36 W/cm² from improvements to cathode and interconnect system.](image-url)
Figure 6. Performance of LSM/YSZ/Ni-YSZ, LSCF/YSZ/FL(Ni-YSZ), and LSCF/ScSZ/FL(Ni-YSZ) cells using hydrogen as fuel.

A 5-cell stack was built of LSCF/YSZ/multilayered (Ni-YSZ) single cells of 5 x 5 cm² and STS 430 interconnects, as shown in Figure 7 (a). At an operating temperature of 650°C, stable stack performance was attained for over 3000 hr. However, some parts of the sealing technology remain unresolved, and stack performance fell short of target at 650°C.

LSCF/ScSZ/Functional-Layered (Ni-YSZ) Cells and Stacks

Recently, Sc-doped zirconia (ScSZ) has received interest for its high ionic conductivity compared to YSZ without significant effects of other characteristics such as chemical stability, compatibility of TEC, and so forth. To improve cell performance further at intermediate temperatures, we adopted ScSZ as electrolyte (6). In the same way, a thin and relatively dense FL of anode was fabricated between ScSZ and the supportive anode plate to improve anode activity, as shown in Figure 5(b). Using ScSZ instead of YSZ as an electrolyte, we achieved another great advance in cell performance, as shown in Figure 6. At 750°C, the ScSZ sample shows a high power density of 1.7 W/cm² at 750°C and 0.55 W/cm² at 650°C.

Maximum power density could not be measured due to our facility's limit of 750°C. Area-specific resistance was reduced from 0.22 to 0.15 ohm cm² at 750°C and from 0.5 to 0.34 ohm cm² at 650°C by changing the electrolyte from YSZ to ScSZ. The polarization loss from electrodes was reduced by changing the electrolyte system (6). Several reports have been written about electrolyte effect for electrode, and our cell shows this kind of behavior. Further investigation is required to fully explain this issue. The LSCF/YSZ/(functional-layered Ni-YSZ) and LSCF/ScSZ/(functional-layered Ni-YSZ) single cell performance showed a maximum power density of 1.2 and 1.7 W/cm² at 750°C, respectively, and 0.36 and 0.55 W/cm² at 650°C. ScSZ electrolyte cell performance was 50% better than the YSZ system increase due to lower ohmic and electrode polarization.
As shown in Figure 7 (b), a 5-cell stack was built using STS 430 interconnects and LSCF/ScSZ/multilayered (Ni-YSZ) single cells of 10 x 10 cm², which is the applicable size for the 1-kW-class RPG system. At an operating temperature of 650°C, stable stack performance was obtained for over 5000 hr. Long-term stack performance was monitored, as shown in Figure 8 (a). Current density of 0.1 A/cm² or 0.2 A/cm² was constant and stack voltage measured. Stack performance sharply decreased after the first 400 hr at 0.2 A/cm² and stabilized after that.

Figure 7. Photographs of short stack at 650°C (STS 430 used as interconnects).

When long-term stack performance at 650°C was examined, as seen in Figure 8 (a), the initial degradation of the stack was determined to be due mainly to performance degradation of each cell rather than oxidation of interconnects (STS 430) at cathodes. Figure 8 (b) shows the same tendency of individual cells when long-term performance without interconnect materials was monitored. Although the single LSCF/ScSZ/FL(Ni-YSZ) cell performed better, its long-term stability seems lower due to thermodynamic instability of scandia stabilizer doped in zirconia, which changes the ionic conductivity of zirconia electrolyte. But after about 4700 hr, each cell and/or stack was more uniform.

The results ensure successful SOFC performance in the intermediate temperature range (especially 650°C) with stainless steel interconnects. After 4700 hr, the operating temperature of the stack was increased to 700°C, which is reasonable for our actual RPG system. More advanced approaches for components (single cells, interconnects, sealing materials) and stack design such as manifold, pressure drop, and flow paths are required.

Figure 8. Performance of (LSCF/ScSZ/FL(Ni-YSZ), 650°C (STS 430 used as interconnects in 5-cell stack).
CONCLUSIONS

Anode-supported SOFCs were developed to ensure high efficiency and performance at intermediate temperatures. To obtain better performance, LSCF composite cathode and ScSZ were used as cathode and electrolyte. When hydrogen was used as fuel, the traditional LSM/YSZ/Ni-YSZ system showed a relatively lower maximum power density of 0.33 W/cm² at 750°C and 0.1 W/cm² at 650°C but excellent long-term performance (over 3 years or 26,000 hr), with a degradation rate of 0.5%/1000 hr. The performance of LSCF/YSZ/(functional-layered Ni-YSZ) and LSCF/ScSZ/(functional-layered Ni-YSZ) single cell showed a maximum power density of 1.2 and 1.7 W/cm² at 750°C and 0.36 and 0.55 W/cm² at 650°C. ScSZ electrolyte cell showed a 50% performance increase due to lower ohmic and electrode polarization compared to the YSZ system. From these results, the oxidation of stainless steel interconnects can be greatly reduced with significant cell efficiency within the temperature range studied.

Fifteen- and 60-cell stacks were constructed based on single cell performance using Inconel as interconnect material. The 15-cell stack showed stable performance over 8,000 hr at 750°C. A sharp performance degradation at the initial state is considered due to oxidation of interconnects. On the basis of investigations for the single cell, a 5-cell stack was built using improved cells (5 x 5 and 10 x 10 cm², respectively) and STS 430 as interconnects to operate at 650°C. The result shows a very good possibility of intermediate temperature SOFC operation using stainless steel and LSCF as interconnect and cathode material, respectively, on YSZ (or ScSZ) electrolyte. From these results, the oxidation of stainless steel interconnects can be greatly reduced with significant cell efficiency within the temperature ranges. This may ensure successful development of a SOFC (RPG) system for intermediate temperature operation.

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