DEVELOPMENT OF KW-CLASS PLANAR SOFC STACKS OPERABLE UNDER FAST THERMAL CYCLES

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ABSTRACT
We have been developing anode-supported planar SOFCs suitable for reduced temperature operation, employing low-cost manufacturing processes. The basic design which utilizes metallic foils for assembling a stack was shown viable for mitigating thermal stresses under fast thermal cycles. A surface modification of the metallic interconnectors successfully prevented the initial degradation of the stack performances. Further, a new stack design suitable for reducing the use of alloy was developed. The 20-cell stack with 13 cm x 13 cm cells, which will be a part of a kW-class stack being tested hereafter, was operated with little voltage deterioration and no destruction of cells was observed after thermal cycles at a heating rate of 200 K/h.

INTRODUCTION
SOFCs with supported electrolyte films have some advantages compared to self-supporting ones. The lower ohmic loss permits a reduction in operating temperature, which further enables us to utilize metallic components for assembling stacks. We have been conducting research and development of anode-supported planar SOFCs combined with alloy stack components to establish mechanical and thermal reliability of stacks. A low-cost manufacturing process for anode-supported SOFCs has been developed, and we have succeeded in fabricating anode-supported SOFCs with an electric conversion efficiency as high as > 50 % HHV at around 1023 K [1].

Two major problems have to be solved in using alloy interconnectors for SOFC stacks. One is degradation of cathode by chromium poisoning [2-5]. Most alloys prepared for high-temperature application against oxidation form the scale of chromium oxide (Cr₂O₃), which generates a vapor of chromium oxyhydroxides during SOFC operation. The vapor was found to deposit around cathode / electrolyte interface to form chromium oxide, which prevents cathode reactivity. The other problem is mismatch of thermal expansion coefficients (TECs) between alloys and cells. In general, metallic materials have larger TECs than the cells. We have developed unique stack structure which mitigates stresses caused by the TECs difference [6].

This paper reports our recent progress in the development of anode-supported planar SOFCs and stacks with metallic components operated at reduced temperatures and under fast thermal cycle conditions.
PERFORMANCE OF SINGLE CELLS

Anode-supported single cells were fabricated by co-firing method, details of which are described elsewhere [6]. Coated YSZ slurry on a compacted substrate of anode precursor was co-sintered, followed by screen-printing and firing of cathode. Anode functional layer made of Ni/YSZ was formed between the anode substrate and the electrolyte to improve reactivity. For cathode, several techniques were employed to prevent chromium poisoning. A samaria-doped ceria (SDC) interlayer was inserted between the electrolyte and the cathode, and (La,Sr)(Co,Fe)O$_3$ was selected for the cathode material, which has higher reactivity at reduced temperatures as well as superior durability against chromium poisoning than the conventional (La,Sr)MnO$_3$ cathodes.

Single cells were scaled-up to as large as 14 cm x 14 cm in size. However, enlargement in the size of the cell was accompanied by a problem of warp as seen in Fig. 1 (a), that originated from the slight difference of TECs among the cell component materials. Cells with relatively large degree of warp can make it difficult to be assembled in a stack with low contact resistance and without a possible destruction of the cells under a certain load. Recently we have modified the fabrication process to reduce the warp. Thus obtained single cell has almost flat surface as seen in Fig. 1 (b).

Performances of the single-cells were monitored at 1023 K using dry and 20% humidified hydrogen as a fuel. They are plotted in Fig. 2, which shows that the performance of the larger cell is inferior to the smaller one but still a voltage over 0.8 V was obtained at 0.2 A/cm$^2$.

![Figure 1. Appearance of single 13 cm x 13 cm cells: (a) before, and (b) after modification of fabrication method.](image)

![Figure 2. I-V characteristics of single cells.](image)
STACK PERFORMANCE

Fig. 3 schematically illustrates the stack structure with alloy interconnectors and manifolds developed for mitigating thermal stresses. The alloy manifold was bonded indirectly with the single cell through thin and flexible metallic foil. The single cell with the alloy manifold is sandwiched between metallic interconnectors having an embossed or grooved structure. All components other than the single cell are made of alloy based on a ferritic stainless steel which has sufficient oxidation resistance even under the cathode condition.

![Figure 3. Schematic illustration of basic stack structure with alloy interconnectors and manifolds developed for mitigating thermal stresses.](image)

The fuel utilization ($U_f$) dependencies of the single cell stack voltages are shown in Fig. 4. The stack voltage of 0.76 V @ 0.2 A/cm$^2$ at $U_f = 86\%$, giving DC energy conversion efficiency of 44.7\% HHV was obtained using 5 cm x 5 cm cell with a fuel of 20\% humidified hydrogen, and for the direct internal reforming of methane (S/C = 2) the voltage was 0.75 V @ 0.2 A/cm$^2$ at $U_f = 85\%$, which corresponds to the efficiency of 55.4\% HHV. The stack voltage of the 11 cm x 11 cm cell was 0.71 V @ 0.2 A/cm$^2$ at $U_f = 88\%$ using dry hydrogen as a fuel, and the calculated conversion efficiency is 42.5\% HHV. The difference of the stack performances between the small and large cell stacks, which was also seen in Fig. 2, is considered to be due to the differences in both contact resistance and fuel distribution to a whole cell.

Thermal-cycle tests between room-temperature and 1023 K with a heating rate of 200 K / h were examined. Fig. 5 (a) shows the plots of open circuit voltage (OCV) in a 10-cell stack with 5 cm x 5 cm cells, and Fig. 5 (b) shows the voltage under a current density of 0.2 A/cm$^2$ of a single cell stack with an 11 cm x 11 cm cell. No drop in OCV was observed, and calculated mean degradation rate of the stack voltage under polarization was 0.48\% / cycle. There were no cracks in the cells of every layer of the stack after the test. These results indicate that our stack structure effectively mitigates thermal stresses, and electrical contact between the cathode and interconnectors remains sufficient even after the thermal cycles.
Figure 4. Fuel utilization dependencies of the voltage of single cell stacks.

Figure 5. Plots of (a) an open circuit voltage in a 10-cell stack with 11 cm x 11 cm cells, and (b) a stack voltage with an 11 cm x 11 cm cell at a current density of 0.2 Acm$^{-2}$, versus number of thermal cycles between room temperature and 1023 K at a heating rate of 200 K/h.

Long-term durability of the single cell stacks of 5 cm x 5 cm cells was examined under a constant current density and plotted in Fig. 6. A large degradation rate was obtained with the stack having the untreated interconnector (A), which indicates incomplete prevention capability of SDC interlayer against Cr-poisoning. Two kinds of coating methods onto metallic components were tried. The areas which do not participate in electrical conduction were coated by an insulating material in order to decrease the absolute quantity of Cr-vaporization (B). Next, a (La, Sr)CoO$_3$ was coated on the interconnector (C), which was reported to be effective in reducing Cr-poisoning [7]. Both stacks were operated stably, and the degradation rate was less than 5% / 1000h with the stack B after operation over 1600 h. Recently, we have adopted a certain technique for the surface modification of the interconnector (D), and succeeded in operation with very little degradation rate over 1500 h.
Figure 6. Time dependencies of stack voltage with 5 cm x 5 cm single cells.

The $I$-$V$ characteristics for a single cell stack and a 10-cell stack at 1023 K are plotted in Fig. 7. A sufficiently high performance was obtained for a large cell stack, and the average voltage over 0.7 V/layer @ 0.2 A/cm$^2$ was achieved.

Figure 7. $I$-$V$ characteristics of a single cell stack and 10-cell stack with 13 cm x 13 cm single cells.

Recently, we developed a new stack design for the purpose of improving reliability against thermal shock, as well as a reduction in the consumption of alloy components. In this stack, as schematically illustrated in Fig. 8 (a), a cell is sandwiched by two sheets of metallic foil and embedded in a manifold, and the interconnector is also made of corrugated metallic foil. Fig. 9 shows $I$-$V$ characteristics of each layer in a 7-cell stack of 13 cm x 13 cm cells. A comparable performance to the conventional stacks was successfully obtained. Also, resistance against fast thermal cycles was demonstrated as seen in Fig. 10, using 20-cell stack of 13 cm x 13 cm cells. For a kW-class operation, examinations of modules composed of multiple 20-cell stacks are underway.
Figure 8. (a) Schematic illustration and (b) assembling manner of the new stack.

Figure 9. $I$-$V$ characteristics of a 7-cell stack with 13 cm x 13 cm cells.

Figure 10. Plots of open circuit voltage in a 20-cell stack with 13 cm x 13 cm cells versus number of thermal cycles between room temperature and 1023 K at a heating rate of 200 K/h.
SUMMARY

Stacks of anode-supported single cells combined with metallic interconnectors and manifolds which can be operated at a reduced temperature have been designed and manufactured. Large single cells having a sufficient flatness have been successfully fabricated. High conversion efficiency over 55% HHV was achieved with methane fuel at 1023 K. No cracking of the large cells in the stacks was observed after thermal cycles at a heating rate of 200 K/h. An excellent long-term durability of the stack with almost no degradation of the stack voltage was achieved.

ACKNOWLEDGMENTS

Part of this work was performed as R&D program of New Energy and Industrial Technology Development Organization (NEDO). We would like to thank NEDO and Ministry of Economy, Trade and Industry (METI) for their advice and financial support.

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