ANODE SUPPORTED INTERCONNECT FOR ELECTROLYTE MEMBRANE SOFC

Kenji Yasumoto, Hibiki Itoh, and Tohru Yamamoto
Smart Materials Science Department, Central Research Institute of Electric Power Industry
2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan

ABSTRACT

Because the contact between anode and interconnect is very important for SOFC stack, we tried fabricating the anode supported interconnect for electrolyte membrane SOFC. Migration of Ca from (La,Ca)CrO$_3$ interconnect to YSZ of Ni-YSZ anode was one of the big problems in the co-firing cell fabrication process because it prohibits the sintering of the interconnect. So, we fabricated the SOFC cell with an interlayer between anode and interconnect. The cells were prepared with a slurry-coating technique starting from YSZ, (La,Ca)(CrCo)O$_3$, and a interlayer material. The cell gave successful results for its dense interconnect protected from Ca migration. It showed a power density of about 0.4 W/cm$^2$ at 1273 K. The electrolyte and electrode reaction resistances of the cell were found larger than interconnect resistance. The concept of anode supported interconnect was proved possible.

INTRODUCTION

In order to commercialize solid oxide fuel cells (SOFC), both the reduction of fabrication costs (1) and achievement of a higher and more stable performance level are necessary. In the research and development of SOFCs at CRIEPI, we have proposed a new concept for the microstructure of anodes, nickel (Ni) and yttria stabilized zirconia (YSZ) cerments, referred to as “YSZ-supported anodes” (2-6). A feature of this material is that, unlike other cerments, the YSZ grains are divided into coarse and fine particles. The cerments have improved long-term stability without reducing the electrochemical performance.

On the other hand, the contact between electrodes (anode and cathode) and interconnect becomes an important problem when stacks are considered. Although the most part of the voltage drop due to the contact resistance comes from the anode electrode side (7), the anode supported interconnect cell has not been successfully fabricated, because alkaline earth doped lanthanum chromite of the interconnect material could not be densified when it was co-fired.
with YSZ (8,9). Furthermore, alkaline earth doped lanthanum chromite is known to be poorly sinterable in air because of the high vapor pressure of Cr (VI) containing species (10). Recently, however, Sakai et al. (11) have reported that Ca doped lanthanum chromite, (La,Ca)CrO$_3$, can be densified in air when a slightly excess amount of Ca was doped. In addition, densification of La$_{0.7}$Ca$_{0.3}$CrO$_3$ (+0.03Ca) proceeds even at 1570 K if material powder was prepared carefully (12). As for co-firing, Kawada et al. (8,9) have reported that migration of Ca from (La,Ca)CrO$_3$ to YSZ was one of the biggest problems in the co-firing process because it prohibits the sintering of the interconnect.

In this paper, in order to fabricate an anode supported interconnect for electrolyte membrane SOFCs, a material with sufficient electrical conductivity was used between the anode and the interconnect to protect them from solid reactions and/or chemical diffusion. The performance of the obtained cell was examined and good results achieved.

**EXPERIMENTAL**

The powders of interconnect materials, Ca and Co doped lanthanum chromite (La,Ca)(Cr,Co)O$_3$, coded as LCCC, were supplied by a chemical corporation in Japan. An interlayer between anode and interconnect was used, and we will report the detail of the interlayer in the near future.

The preparation procedure for the YSZ-supported anode consists of two main steps. The first step is the control of the particle size distribution, and the second is the mixing of the powders. Details of this process have been described elsewhere (2-6). The present sample used the coarse YSZ (27.0 \( \mu \)m), the NiO (1.0 \( \mu \)m), and the fine YSZ (0.6 \( \mu \)m) in the weight ratio 4:6:1. The powder was mixed, pressed, and sintered in air at 1673 K into pellets of about 20 mm in diameter and about 2 mm in thickness for anode / interconnect cells (cell-A1 and 2). The same sintering temperature, 1673 K, was adopted for making a block, which, after cutting, resulted in 30 mm \( \times \) 30 mm \( \times \) 10 mm anode support for a cathode / electrolyte / anode / interconnect cell (cell-B).

An interlayer material was slurry-coated on one side of the anode electrode bases (cell-A1 and B) and fired at 1673-1723 K. Here, the cell-A2 was not coated with interlayer in order to serve as a reference to observe the effect of the interlayer. The interconnect material was slurry-coated on the cell-A1 and 2 and cell-B, and fired at 1673-1723 K. The process was repeated several times to make the interconnect thick enough. For cell-B, YSZ was slurry-coated on the opposite side and fired at 1673-1723 K. Then, Sr doped lanthanum manganite cathode of 4 cm$^2$ in square shape was printed by tape casting on the YSZ of the cell-B, and fired at 1423 K for 1 h. Finally, Pt mesh was attached to cathode (as the working electrode, WE, and the reference electrode, (RE), anode (as the RE), and interconnect (as the counter electrode, CE, and the RE) of the cell B using Pt past, and fired at 1273 K for 1 h.
Schematic drawing of the configuration of the cell-B is shown in Fig. 1 (a).

The structure properties for the cell-A was investigated by a scanning electron microscopy, SEM, and an electron probe micro analyzer, EPMA, (JEOL Ltd., JXA-8900R). The electrochemical performances at 1273 K were examined by DC polarization measurement using a charge / discharge unit (Hokuto Denko, HJ-2010) and by AC impedance measurement in the frequency range of 100 kHz to 1 mHz using a frequency analyzer (SOLARTRON, SI 1260), a potentiostat (SOLARTRON, SI 1287), and a personal computer. The setup for the electrochemical measurements is schematically shown in Fig. 1(b). In the electrochemical measurements, gaseous H₂ humidified by water at 293 K (350 ml/min) as a fuel and dry air (1000 ml/min) as an oxidant were supplied to the anode and the cathode, respectively.

RESULTS AND DISCUSSION

In order to investigate the anode / interlayer / interconnect condition more closely, a cross section of the cells A1 and A2 are observed by SEM. Figures 2(a) and (b) show the cross section SEM images of the cell A1 and A2, respectively. The cell A1 was coated with an interlayer; the cell A2 was not. The SEM images indicate that the interconnect / interlayer membrane of cell A1 (Fig. 2(a)) became dense, but interconnect of cell A2 (Fig. 2(b)) was porous. We attribute the porous structure to the migration of Ca of LCCC to YSZ as reported by Kawada et al. (8, 9). From Fig. 2, the thickness of the obtained interconnect / interlayer membrane of cell A1, and interconnect membrane of cell A2 are about 10 µm and 20 µm, respectively. For cell A1, the interface between interconnect and interlayer was not observed in this SEM image of Fig. 2(a). Accordingly, we investigated the distribution of all chemical elements for cells A1 and A2 by EPMA. We focused on Ni, La, Zr, Y, Cr, Ca, and a chemical element (X) of interlayer in the anode / interlayer / interconnect structure of cell A1 and the anode / interconnect interface, as shown in Figs. 3 and 4, respectively. Here elements of less content and part of those in interlayer were not shown in Fig. 3. We observed that Ca of LCCC migrated to YSZ in cell A2, as shown in Fig. 4, but did not migrate in cell A1, as shown in Fig. 3. Because cell A2 was coated with the interlayer, migration of Ca from LCCC to YSZ is prevented. Note that the thicknesses of the obtained interlayer and interconnect membrane are about 2 and 8 µm, respectively.

We succeeded in fabricating the dense interconnect on anode. The anode supported interconnecting electrolyte membrane SOFC, cell B, was examined with humidified hydrogen as fuel and air as oxidant at 1273 K. Figure 5 shows the relationships between current density and cell voltage and those between current density and power density measured on cell B with or without interconnect/interlayer membrane contribution at 1273 K. As seen in Fig. 1(a), there are three RE for examining the voltage drop across the interconnect / interlayer membrane and measuring the cell performance without such voltage drop. We attribute both the
interconnect and the electrolyte of cell B were dense enough, because the open circuit voltage (OCV) is about 1.0 V. The cell B showed the maximum power density of about 0.4 W/cm\(^2\) at about 0.8 A/cm\(^2\). Although the voltage drop across the interconnect/interlayer membrane is small, the performance for cell B is lower than that of a similar cell without interconnect reported in previous papers (13, 14).

Figure 6 shows the complex impedance plots of cell B using humidified hydrogen as fuel and air as oxidant at 1273 K when the electrical potential was measured between cathode and interconnect (a), between cathode and anode (b), and between anode and interconnect (c), respectively. Here, WE and CE are connected to the cathode and interconnect, respectively. We found three impedance components, with the real part resistance \(R_{\text{b}}\), \(R_{\text{EI}}\), and \(R_{\text{E2}}\), for cells (a) and (b) shown in Fig. 6. But only one impedance component, with the real part resistance \(R_{\text{b}}\), was obtained for cell (c). The interconnect/interlayer membrane resistance, ca. 0.12 \(\Omega\)-cm\(^2\) from \(R_{\text{b}}\) of cell (c), is smaller than that across electrolyte, ca. 0.22 \(\Omega\)-cm\(^2\) from \(R_{\text{b}}\) of cell (b), and that due to electrode reactions, ca. 0.5 \(\Omega\)-cm\(^2\) from \(R_{\text{EI}} + R_{\text{E2}}\) of cells (a) and (b). As for \(R_{\text{b}}\), we think the anode base resistance is small as reported in our work (6). As for \(R_{\text{EI}}\) and \(R_{\text{E2}}\), because our experimental device can't be changed to other gas conditions, \(R_{\text{EI}}\) and \(R_{\text{E2}}\) can't be separated in anode and/or cathode resistances; however, they are much the same.

Figure 7 shows the relationships between current density and cell voltage, and voltage drops across the interconnect/interlayer and electrolyte membranes of the cell B at 1273 K. From Fig. 7, voltage drops across the electrolyte and on electrodes are large. As for electrolyte, in order to avoid failures of cell fabrication, we fabricated the electrolyte film thick. Therefore, we can understand its large voltage drop. However, this is not a big problem, because we can fabricate thin electrolyte film as reported in our previous works (13, 14). As for voltage drop of electrode reactions, the performance is not satisfied. Consequently, the electrode activities must be improved in the future.

**SUMMARY**

The anode supported interconnect for electrolyte membrane SOFC was investigated. We fabricated the SOFC cell with an interlayer between anode and interconnect to protect (La,Ca)CrO\(_3\) interconnect from migration of Ca. The cell gave successful results for its dense interconnect, and showed the maximum power density of about 0.4 W/cm\(^2\) at about 0.8 A/cm\(^2\). The voltage drop of the interconnect/interlayer membrane was small, but those of electrolyte and electrode reactions were large. The results suggested that it was possible to fabricate the anode supported dense interconnect with the help of an interlayer for the electrolyte membrane SOFC.
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Figure 1. Schematic illustration of a cell shape and experimental setup for electrochemical measurements.

Figure 2. Cross-sectional SEM images of the anode / interconnect interface with (A1) or without (A2) the interlayer for cell-A.
Figure 3. The distributions of Ni, Zr, La, Ca, and a chemical element (X) of interlayer across the anode / interconnect interface of Cell-A1.

Figure 4. The distributions of Ni, Zr, La, Ca, and a chemical element (X) of interlayer across the anode / interconnect interface of Cell-A2.
Figure 5. Relationships between current density and cell voltage (the closed symbols), and between current and power densities (the open symbols) measured with (○○) or without (△△) interconnect/interlayer membrane contribution for the cell-B at 1273 K.

(a) Cathode/YSZ/Anode/I.L./I.C.
(b) Cathode/YSZ/Anode
(c) Anode/I.L./I.C.

Figure 6. Complex impedance plots of cell-B using humidified hydrogen as fuel and air as oxidant at 1273 K when the electrical potential was measured between cathode and interconnect (a), between cathode and anode (b), and between anode and interconnect (c), respectively. Here, WE and CE are connected to the cathode and interconnect, respectively.
Figure 7. Voltage drop due to the YSZ resistance (IR1), the interconnect resistance (IR2), and the electrode reactions (IR3) for the cell-B at 1273 K.