RESEARCH AND DEVELOPMENT OF ANODE SUPPORTED INTERCONNECT FOR SOFC

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ABSTRACT
Because the contact between anode and interconnect is very important for SOFC stack, we tried fabricating the anode supported interconnect for SOFC. Migration of Ca from (La,Ca)CrO₃ 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)(Cr,Co)O₃ and interlayer materials, (Ce,Y)O₂, Ca(Ti,Nb)O₃, or another material. Three kinds of cells gave successful results for their dense interconnects protected from Ca migration. The cell of a material interlayer / (La,Ca)(Cr,Co)O₃ / (La,Sr)MnO₃ interconnect showed a power density of 0.85 W/cm² (0.7 V) at 1273 K. The concept of anode supported interconnect was shown possible.

INTRODUCTION
In order to commercialize solid oxide fuel cells (SOFCs), 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 anode, nickel (Ni) and yttria stabilized zirconia (YSZ) cermets, referred to as "YSZ-supported anodes" (2-6). A feature of this material is that, unlike other cermets, the YSZ grains are divided into coarse and fine particles. The cermets have improved long-term stability without reducing the electrochemical performance.

The contact between electrodes (anode and cathode) and interconnect becomes an important problem when stacks are prepared. Although the largest part of the voltage drop due to contact resistance comes from the anode 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)CrO₃, can be densified in air when a slightly excess amount of Ca was doped. In addition, densification of L₄₀₀₇Ca₀₃CrO₃ (+0.03Ca) proceeds even at 1570 K if material powder is prepared carefully (12). As for co-firing,
Kawada et al. (8, 9) have reported that migration of Ca from (La,Ca)CrO₃ to YSZ was one of the biggest problems in the co-firing process because it prohibits sintering of the interconnect.

On the other hand, Ca doped lanthanum chromite, (La,Ca)ₐ₋₁CrO₃, is known to form calcium chromate hydroxyl apatite, Caₙ(CrO₄)₂OH, at high temperatures with high humidity (13). By the formation of the Caₙ(CrO₄)₂OH, the electrical conductivity of interconnect decreases, and dense bodies of interconnect become porous.

In this paper, in order to fabricate an anode supported interconnect for electrolyte membrane SOFCs, (Ce,Y)O₂, Ca(Ti,Nb)O₃, or a “material” with sufficient electrical conductivity was used as interlayer between the anode and the interconnect, and (La,Sr)MnO₃ was used as protective-layer on the interconnect to protect them from solid state reactions and/or chemical diffusion.

**EXPERIMENTAL**

**Materials**

The powders of interconnect materials, Ca and Co doped lanthanum chromite (La,Ca)(Cr,Co)O₃, were supplied by a chemical corporation in Japan. The interlayer between anode and interconnect as shown in Fig. 1 and Table 1 was (Ce,Y)O₂ supplied by a SOFC group (Cell A), Ca(Ti,Nb)O₃ synthesized by traditional ceramic method (Cell B), or a proprietary “material” (Cell C); we will report details of the “material” in the near future. The protective-layer on the interconnect (Cell C) as shown in Fig. 1 (b) and Table 1 was (La,Sr)MnO₃ supplied by a chemical corporation in Japan.

**Cell Preparation**

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 coarse YSZ (27.0 µm), fine NiO (1.0 µm), and fine YSZ (0.6 µm) in the weight ratio 4:6:1. The powders were mixed, pressed, and sintered in air at 1673 K for making a block, which, after cutting, resulted in 30 mm × 30 mm × 10 mm anode support.

The interlayer material was slurry-coated on one side of the anode block and fired at 1673 K. Here, the cell D was not coated with the interlayer in order to serve as a reference to observe the effect of the interlayer. The interconnect material was slurry-coated on the side of interlayer, and fired at 1673 K. The process was repeated several times to make interconnect thick enough. In the case of “material” as interlayer, the protective-layer material was slurry-coated on the side of interconnect as shown in Fig. 1 (b) and Table 1, and fired at 1673 K. The YSZ was slurry-coated on the opposite side and fired at 1673 K. Then, Sr doped lanthanum manganite cathode with 4 cm² in square shape was printed by tape casting on the YSZ electrolyte, 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 using Pt paste, and fired at 1373 K for 1 h. Schematic drawing of the configuration is shown in Fig. 2 (a).
Measurement of Cell Characteristics

The structure properties for each cell were investigated by scanning electron microscopy, SEM, and an electron probe microanalyzer, EPMA, (JEOL Ltd., JXA-8900R). The electrochemical performances at 1273 K were examined by DC polarization measurements using a charge / discharge unit (Hokuto Denko, HJ-2010). The setup for the electrochemical measurements is schematically shown in Fig. 2 (b). In the electrochemical measurements, gaseous H₂ humidified by water at 293 K (0.3 l/min) as fuel and dry air (1.0 l/min) as oxidant were supplied to the anode and the cathode, respectively.

RESULTS AND DISCUSSION

Structure Properties

In order to investigate the anode / interlayer / interconnect condition more closely, cross sections of the cells were observed by SEM. Figures 3 (a) and (b) show the cross section SEM images of the cells A and D, respectively. The cell A was coated with (Ce,Y)O₂ interlayer, while the cell D was un-coated reference. The SEM images indicate that the interconnect / interlayer membrane of cell A [Fig. 3 (a)] became dense, but interconnect of cell D [Fig. 3 (b)] was porous. We attribute the porous structure to the migration of Ca of (La,Ca)(Cr,Co)O₃ to YSZ as reported by Kawada et al. (8, 9). From Fig. 3, the thicknesses of the obtained interconnect / interlayer membrane of cell A, and interconnect membrane of cell D are about 10 μm and 20 μm, respectively. For cell A, the interface between interconnect and interlayer was not observed in this SEM image of Fig. 3 (a). Accordingly, we investigated the distribution of all chemical elements for cells A and D by EPMA. We focused on Ni, Zr, La, Ca, and Ce in the anode / interlayer / interconnect structure of cell A and the anode / interconnect structure of cell D, as shown in Figs. 4 and 5, respectively. We observed that Ca of (La,Ca)(Cr,Co)O₃ migrated to YSZ in cell D, but did not migrate in cell A, as shown in Fig. 4. Because cell D was coated with the interlayer, migration of Ca from (La,Ca)(Cr,Co)O₃ to YSZ is prevented. Note that the thicknesses of the obtained interlayer and interconnect membrane are about 2 and 8 μm, respectively. For the cells B and D, Ca of (La,Ca)(Cr,Co)O₃ did not migrate to YSZ and counter diffusion between (La,Ca)(Cr,Co)O₃ interconnect and (La,Sr)MnO₃ protective-layer did not occur. We succeeded in fabricating the dense interconnect on anode.

Cell Performance

Cells B and C were examined with humidified hydrogen as fuel and air as oxidant at 1273 K. Figures 6 and 7 show the relationships between current density and cell voltage, those between current density and power density, and voltage drops across the interconnect membrane [the voltage between RE 3 and RE 4 as shown in Fig. 2 (b)] and those of the anode reaction [the voltage between RE 2 and RE 3] and cathode reaction [the voltage between RE 2 and RE 1] measured on cells B and C at 1273 K, respectively. The interconnect and the electrolyte of cells B and C were dense enough, because the open circuit voltage (OCV) is 1.0 V and over. The cells B and C showed a power density of 0.7 W/cm² and 0.85 W/cm² at about 0.7 V. From Figs. 6 and 7, the voltage drop across the interconnect / interlayer membrane and that of the anode reaction are small. As for voltage drop of the cathode reactions, the performance is not...
Figure 8 shows time dependence of the cell voltage and interconnect overpotential for the cells B and C at 1273 K. The performance of the cell C was twice as high as that of the cell D. Long-term stability of interconnect for the cells B and C was observed, however, that of cell performance is not satisfactory. While long-term stability of anode and electrolyte was attested by reports in our previous work (14), that of cathode is a problem. In present work, we did not experiment in high water containing atmosphere of air in order to examine the effect of protective-layer. Consequently, the electrode activity and long-term stability of cathode must be improved in the future.

**SUMMARY**

Anode supported interconnect for electrolyte membrane SOFC was investigated. We fabricated a cell with an interlayer between anode and interconnect to protect (La$_3$Ca)CrO$_3$ interconnect from migration of Ca. The cell gave successful results for its dense interconnect, and showed a maximum power density of 0.85 W/cm$^2$ at about 0.7 V. The voltage drops across the interconnect / interlayer and the electrolyte membranes and of anode reaction were small, but that of cathode reaction was large. The results suggest that it is possible to fabricate anode supported dense interconnect with an interlayer for the electrolyte membrane SOFCs.

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![Diagram](image1)

Figure 1. Schematic image of interconnect on anode substrate.

Table 1. Constituent materials of Anode / Interlayer / Interconnect / Protective-layer.

|                | Cell A | Cell B | Cell C | Cell D |
|----------------|--------|--------|--------|--------|
| Anode          | Coarse YSZ (27.0 μm) : NiO (1.0 μm) : Fine YSZ (0.6 μm) = 4 : 6 : 1 |
| Interlayer     | (Ce,Y)O₂ | Ca(Ti,Nb)O₃ | A material | Nothing |
| Interconnect   | (La,Ca)(Cr,Co)O₃ |
| Protective-layer | Nothing | Nothing | Nothing | (La,Sr)MnO₃ |

![Diagram](image2)

Figure 2. Schematic illustration of a cell shape and experimental setup for electrochemical measurements. WE, CE, and RE are the working, counter, and reference electrodes.
Figure 3. Cross-sectional SEM images of the anode / interconnect interface with (cell A) / without (cell D) the (Ce,Y)O$_2$ interlayer.

Figure 4. The distributions of Ni, Zr, La, Ca, and Ce across the anode (Ni-YSZ) / interlayer [(Ce,Y)O$_2$] / interconnect [(La,Ca)(Cr,Co)O$_3$] interface of Cell A.
Figure 5. The distributions of Ni, Zr, La, and Ca across the anode (Ni-YSZ) / interconnect [(La,Ca)(Cr,Co)O3] of Cell D.

Figure 6. Relationships between current density and cell voltage (the open circle symbols), and between current density and power density (the closed circle symbols) and voltage drop due to the Interconnect (I), the anode (II), and the cathode (III) resistances for the cell B, the anode (Ni-YSZ) / interlayer [Ca(Tl,Nb)O2] / interconnect [(La,Ca)(Cr,Co)O3], at 1273 K.
Figure 7. Relationships between current density and cell voltage (the open circle symbols), and between current density and power density (the closed circle symbols) and voltage drop due to the Interconnect (I), the anode (II), and the cathode (III) resistances for the cell C, the anode (Ni-YSZ) / interlayer [a material] / interconnect [(La,Ca)(Cr,Co)O₃] / protective-layer [(La,Sr)MnO₃], at 1273 K.

Figure 8. Times dependence of the cell voltage and interconnect overpotential for the cells B and C at 1273 K.