PERFORMANCE CHARACTERISTICS OF PLANAR SOLID OXIDE FUEL CELLS FABRICATED BY COMPOSITE PLATE PROCESS

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ABSTRACT

The composite plate process has been investigated, in which green films were co-fired in the forms of two layers of anode/electrolyte and of three layers of anode/electrolyte/cathode attached with gas distributors. The flat cell of 83 cm² was fabricated successfully. For characterizing its performance, the single cells with an effective area of 1.25 cm² were tested. In the small size cell test, the co-fired cell of two layers showed higher performance than that of three layers. The performance loss in the co-fired cell of three layers was due mainly to large iR drop in the cathode gas distributor. The co-fired cell of two layers yielded a power density of 200 mW/cm² at 328 mA/cm². On the basis of these results, some problems of the composite plate process were discussed.

INTRODUCTION

Planar solid oxide fuel cells (SOFCs) are very attractive because of high efficiency, simple cell structure and potential for large scale power plants. For low cost production of the planar SOFC, much attention has been paid to tape cast methods such as doctor blade, by which one can easily fabricate an electrolyte and an interconnector as non-supported films(1,2). After tape cast, the individual components are usually sintered at different temperatures and then are assembled as one cell. However, the non-supported films produced by this process are difficult to handle because of their fragility, and this method requires many sintering steps for making cells.

To overcome these problems, many investigators have studied co-firing processes(3,4). In a conventional co-firing process, the four green films that consist of anode, cathode, electrolyte and interconnector are co-fired for making cell. This method has the following disadvantages: the difficulty in fabricating large cells, the Ca migration from the interconnector and the Mn diffusion from the cathode to YSZ(5,6).
In this study, we have investigated a composite plate process to develop the efficient fabrication technology of the planar SOFC, in which green films were co-fired in the forms of two layers of anode/electrolyte and of three layers of anode/electrolyte/cathode with gas distributors. Cells composed of the co-fired layers were tested for characterizing the performance by the current interrupt and the ac impedance methods. Some problems in the composite plate process were also discussed.

EXPERIMENTAL

The electrolyte powder was 8 mol.% yttria-stabilized zirconia (YSZ) supplied by TOSOH Co. (TZ-8YS). The anode material was nickel YSZ cermet (NY) which was prepared by mixing basic nickel carbonate with YSZ in ethanol solution and by drying this mixture at 550 °C. The NY powder had 37 vol.% nickel metal after reduction. The \((\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_3\) (LSM) powder for the cathode was prepared by co-precipitation method; the starting materials were nitrate solutions of La, Sr and Mn. These nitrate solutions were mixed in a proper ratio and poured into an ethanol oxalic acid solution. After being dried, the precipitates were calcined at 1000 °C for 5 h. The \(\text{La}_{0.67}\text{Ca}_{0.33}\text{CrO}_3\) (LCC) powder used as interconnector was prepared by a ceramic method. The powders were calcined two times at 1000 °C for 15 h.

The doctor blade method was used for making green films. The slurries of electrolyte and electrodes were prepared by mixing each powder in pot ball mill for 24 h with organic substances that include polyvinyl butyral, dibutyl phthalate, polyethylene glycol mono-p-isooctyl phenyl ether (Triton-X), fish oil, toluene, and isopropyl alcohol. Two types of single cell were considered in this study. One was made by co-firing a layered green film of anode, electrolyte and cathode with two green foam plates of gas distributor. Hereafter we call this type "co-fired cell of three layers." The three layered green films were made sequentially by doctor blade method. The gas distributor was prepared from polyurethane foam plate, dipped with YSZ slurry in order to give similar shrinkage to YSZ electrolyte. The gas distributors were attached to both anode and cathode sides of the green three layers. The other was made by co-firing two layers of anode and electrolyte with a gas distributor. Hereafter this type is named as "co-fired cell of two layers." The gas distributor was attached to only anode side of green two layers.

All the green cells were burnt out at 350 °C, followed by sintering at 1380 °C for 3 h in air. The size of the sintered cell was 10.8×7.7 cm²; the shrinkage was 23 %. The sintered cells were always warped, and thus flattening was carried out by heating the warped cells again at 1380 °C for 3 h with some weights. After sintering, the gas distributors consisted of a very porous YSZ material, were not electronically conductive. Thus additional treatments were carried out in order to impart electronic conduction to the gas distributor. The gas distributors for the anode and the cathode were impregnated with NiO and LSM slurries, respectively. All the cells were sintered again at 1380 °C for 3 h. After these processes the cell of three layers became a complete single cell. On the other
hand, the cell of two layers needs to furnish a cathode for being a single cell. Thus LSM slurry was painted and sintered at 1250 °C for 5 h. The final cell of two layers had a gas distributor only on the anode side.

The single cells of 1.25 cm² were tested. For this test, fragments of the co-fired cells of two layers and three layers were used. Hydrogen with humidity of 3 % and air were supplied without preheating. Flow rates of hydrogen and air were 50 cc/min and 500 cc/min, respectively. The half cell performances of anode and cathode were examined using a reference electrode of platinum exposed to air. The iR drop, and the overvoltages of anode and cathode were evaluated by the current interrupt and the ac impedance methods. The impedance was measured using impedance/gain analyzer(Solartron SI 1260) in the range of 0.1 to 10⁵ Hz with dc bias.

For the preliminary stage of the stack fabrication, the unit cell which is composed of the co-fired two layers' cell of 83 cm² and the bipolar plates, was designed and fabricated.

RESULTS AND DISCUSSION

In order to make a stack, it is required to obtain flat cell components. To avoid a warpage of cell components, the gas distribution plates composed of porous YSZ were adopted instead of using those of NY and LSM. However, the warpage of the sintered cell was inevitable because of different shrinkage behavior at electrodes. In this work the flat cell components with an area of 83 cm² were obtained under pressures of 637 and 802 Pa at a heating rate of 45 °C/min to 1380 °C with holding for 3 h. At low pressure below 483 Pa, a cell component remained warped but, when this cell component was treated again under 1592 Pa, the cell became flat. Some cell components were cracked at heavy weights or high heating rates. These results mean that the applied pressure and the heating rate are important factors in the flattening process.

The performance of a co-fired cell of two layers was measured after operation of 24 h and the result was shown in Fig.1. The iR-included maximum power density attained 200 mW/cm² at 608 mV and 328 mA/cm². The iR losses of the cells were evaluated by a current interrupt method and the iR-free power density was about 400 mW/cm². In Fig.1 it was found that the main performance loss is due to iR drop. Figure 2 shows the performance of a co-fired cell of three layers. The iR drop in the co-fired cell of three layers was much larger than that of two layers.

The polarization characteristic features in the co-fired cell of two layers are illustrated in Figs.3 and 4. The electrode overvoltages were relatively low but a large iR drop appeared in the anodic side. The iR drop of the anodic side may stem from an anode gas distributor, an anode or a current collector. To make clear its origin, additional measurements were made. Figure 5 shows an electrical conductivity of the anode gas distributor as a function of holding time, which was measured in hydrogen atmosphere at
1000 °C. The anode gas distributor has a high electrical conductivity, which produces a low iR drop. The anode has also a high electrical conductivity because of much Ni volume of 37%. Therefore it is thought that the large iR drop in the anodic side came from the current collector. The current collector in the anodic side was composed of Ni felt and Pt mesh; the Ni felt was positioned between anode gas distributor and Pt mesh. Poor contact between the current collector and the anode gas distributor may induce a large iR drop. The cathode side in this cell had no gas distributor. Thus the iR drop in the cathode side is considered to be due to contact resistance between cathode and platinum current collector, which is similar to the case of the anodic side.

The polarization behavior in the co-fired cell of three layers is also presented in Figs. 3 and 4. In contrast to that of two layers, a much larger iR drop existed in the cathodic side, which was found to be due to poor conductivity of the cathode gas distributor, as shown in Fig.6. In the cathode gas distributor, LSM was coated on the skeleton of porous YSZ. The portion of LSM volume was small in comparison with that of YSZ, which results in the large ohmic resistance of the cathodic side. For the cathode gas distributor, it will be required to fabricate it using LSM only. In the anodic part, the iR drop and the overvoltage of the co-fired three layers' cell were similar to those of the co-fired two layers' cell but the cathodic overvoltage of the co-fired three layers' cell was significantly large. The cathode of the co-fired three layers' cell was sintered at 1380 °C that is higher than the sintering temperature of the cathode (1250 °C) in the co-fired two layers' cell. The high sintering temperature may promote a reaction between LSM and YSZ, and the transport of Mn in LSM to YSZ (7). This means loss of cathodic activity, that is, development of a large cathodic overvoltage.

Figure 7 shows the performance of the co-fired cell of two layers as a function of operating time. The cell performance degraded largely after an operation of 150 h. To evaluate the degradation factors, ac impedance was measured and the results were represented in Figs. 8 and 9. The impedance plot indicates that the cell performance decay is due to the increases of both iR drop and electrode overvoltages. Most of iR drop came from the degradation of the anodic side as shown in Fig. 9, which is attributed to the poor contact of the anodic side because the anode and the anode gas distributor are considered to have still high conductivity. The increase of the cell overvoltage originates from both anode and cathode; the anodic overvoltage was larger than the cathodic one. The increase in the anodic overvoltage may be related to the coagulation of Ni particles, etc. (8, 9).

From these results, some problems in the composite plate process are summarized as follows: (1) high cathodic overvoltage of co-fired cathode
(2) poor electrical conductivity of cathode gas distributor.
(3) long-term instability of the anode gas distributor.
(4) poor contact between anodic gas distributor and current collector.
(5) increase of overvoltage at anode.
The high cathodic overvoltage is considered to be due to the reaction of LSM with YSZ. It will be difficult to lower the co-firing temperature. For the co-fired cell of three layers a new cathode material is required, which is endurable to high temperature sintering. The instability of the anode gas distributor arises from the degradation of its electrical conductivity. Although the conductivity of the anode gas distributor remains high within several hundred hours, as shown in Fig. 5, it should be noted that the decay rate is rapid. The remarkable decrease of the electrical conductivity in the anode gas distributor is a serious problem because the fuel cell requires an operation of 40000 h for commercialization.

We think that the problems concerning gas distributor are caused by an insufficient impregnation of the slurries. The stability of the anode gas distributor is likely to be improved in future because the co-fired cell of two layers had good performance at the start of operation. An increase of Ni volume in the anode gas distributor should be attempted in the future work. On the other hand, considering the poor conductivity of YSZ/LSM composite, the LSM impregnation in the cathode gas distributor is thought to be not adequate. Thus the development of a new cathode gas distributor which is composed of only LSM is required. Generally the increase of contact resistance among interconnector, anode gas distributor and anode would be more serious problem than the decrease of the conductivity at anode side. The decrease of contact pressure or the formation of small cracks originates in increases of contact resistance. The improvement is one of common problems at the stacking step of planar cell fabrication. Many authors reported the poor endurance of anode(8,9). It is usually attributed to the morphological changes such as the coagulation of Ni particles, the decrease of three phase boundaries, and the formation of microcracks, etc. For the case of the co-fired anode, these problems remain unsolved for the future work.

From this viewpoint, the co-fired cell of two layers is preferable to that of three layers for making an efficient stack. Using the co-fired cell of two layers, we constructed a unit cell with area of 83 cm² for testing the large cell performance. Its schematic view is presented in Fig. 10. The unit cell is composed of the co-fired cell of two layers, bipolar plates and external gas manifold. The gases are supplied by cross-flow type. To prevent direct contact between bipolar plate and electrodes that may degrade the electrode activities(7,10), porous Ni and LSM plates were inserted into the anodic and cathodic sides, respectively. The porous plates also play a role of gas channels. This unit cell will be used for making a stack. A large cell test and stacking are in progress for examining the applicability of the present composite plate process to the stack fabrication.

CONCLUSION

The composite plate process for fabricating the planar solid oxide fuel cell was investigated. A flat cell of 7.7x10.8 cm² was fabricated successfully by composite plate process. The test results of the small size cells lead to the following conclusions:
(1) A co-fired cell of two layers yielded a power of 200 mW/cm²: 608 mV at 328 mA/cm². Its performance loss was mainly due to iR drop in the anode gas distributor, which was caused by poor contact between anode gas distributor and current collector.

(2) The performance in the co-fired cell of three layers was much lower than that of two layers, which resulted from the large iR drop and overvoltage at the cathodic side.

(3) For future work, the improvement of electrical conductivity of gas distributors, especially the development of the cathode gas distributor with high electronic conductivity is required.

(4) The large unit cell, which is composed of the co-fired cell of two layers, the bipolar plates and the external gas manifold, was constructed. Its performance test and the stack fabrication are in progress.

ACKNOWLEDGMENT

The supports of Japan-Korea Industrial Technology Co-operation Foundation and Korea-Japan Industrial Technology Co-operation Foundation are greatly appreciated.

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Fig. 1 Performance of the co-fired cell of two layers after operation of 24 h. (Δ, ▲) iR-included; (O, ●) iR-free.

Fig. 2 Performance of the co-fired cell of three layers after operation of 24 h. (Δ, ▲) iR-included; (O, ●) iR-free.

Fig. 3 Comparison of electrode overvoltages in the co-fired cells of two layers (O, Δ) and three layers (●, ▲) after operation of 24 h.

Fig. 4 Comparison of iR drops in the co-fired cells of two layers (O, Δ) and three layers (●, ▲) after operation of 24 h.
Fig. 5 Electrical conductivity of the anode gas distributor as a function of holding time. This was measured in H₂ at 1000 °C.

Fig. 6 Electrical conductivity of the cathode gas distributor. This was measured in air under a current density of 62 mA/mm² by four probe method.

Fig. 7 Performance of the co-fired cell of two layers as a function of operating time.
Fig. 8 Impedance plot for the co-fired cell of two layers at two different operating times, which was measured at the direct current of 30 mA.

Fig. 9 Impedance plot for the co-fired cell of two layers measured at the direct current of 30 mA after operation of 150 h.
Fig. 10 Single cell structure composed of the co-fired cell of two layers. This unit cell will be used for making stack.