

Fabrication of Planar Solid Oxide Fuel Cell by Composite Plate Process

Rak-Hyun SONG*, Teruhisa HORITA†, Natsuko SAKAI†, Tatsuya KAWADA†,
Harumi YOKOKAWA† and Masayuki DOKIYA†

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The composite plate process has been investigated, in which the 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 cells of 83 cm² were fabricated successfully. For characterizing its performance, the single cells with an effective area of 1.25 cm² were tested. The co-fired cell of two layers showed higher performance than that of three layers. In the co-fired cell of two layers, the large voltage loss appeared in anodic side after 150 h operation, which is attributed to the poor contact between anode gas distributor and current collector, and to the increase of anodic polarization. On the other hand, the performance loss in the co-fired cell of three layers was due mainly to large iR drop and electrode overvoltage in the cathodic side. On the basis of these results, some problems in the composite plate process were discussed.

1 INTRODUCTION

Solid oxide fuel cell (SOFC) is an electrochemical energy device which converts the free energy of fuel gas directly to electric energy. SOFC has advantages of high efficiency, low pollution and cogeneration application. To date two types of SOFC, which include tubular and planar ones, have been developed mainly for aiming at power plant.^{1,2)} Planar SOFC is very attractive because of higher efficiency, more simple structure and potential for large scale. For fabrication of the planar SOFC, many attentions have been given to tape cast methods such as doctor blade, by which one can easily fabricate electrolyte and interconnector.^{3,4)} 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 is difficult to handle because of its fragility, and this method requires many sintering steps for making cells.

To overcome these problems, many investigators have studied co-firing processes.^{5,6)} 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 in the interconnector and the Mn loss in the cathode.^{7,8)}

In this study, we have investigated the 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. The cells composed of the co-fired layers were tested for characterizing their performance by the current interrupt and the ac impedance methods. Some problems in composite plate process were also discussed.

2 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 (La_{0.85}Sr_{0.15})_{0.9}MnO_{3-δ} (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 composite plate process is represented in Fig. 1. 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

*Korea Institute of Energy Research, (P.O.Box 103, Yusong, Taejon, 305-600, Korea)

†National Institute of Materials and Chemical Research, (1-1, Higashi, Tsukuba, Ibaraki 305, Japan)

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for 24 h with organic substances that include polyvinyl butyral, dibutyl phthalate, polyethylene glycol mono-p-iso-octyl phenyl ether (Triton-X), fish oil, toluene, and isopropyl alcohol. In this study, two types of single cell were fabricated by using the composite plate process. 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.

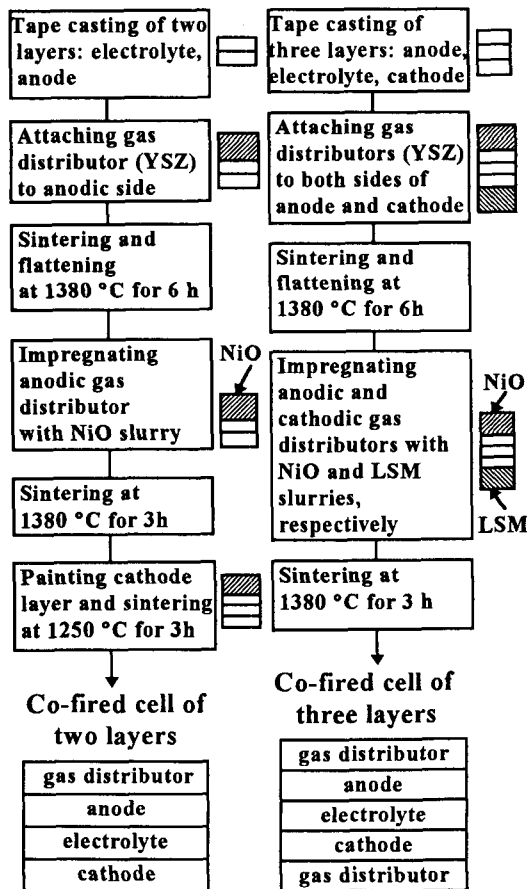


Fig.1 Fabrication of the co-fired cell by composite plate process.

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 %. Thicknesses of electrolyte, cathode, anode, anode gas distributor and cathode gas distributor were 150, 20, 15, 750, 750 μm, respectively. 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 (porosity ca. 80%, diameter of pore ca.0.2mm), 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. However, as is shown later (Fig.7), the amount of LSM was not enough to obtain high conductivity, whereas NiO gave high conductivity as shown later (Fig.6). 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.

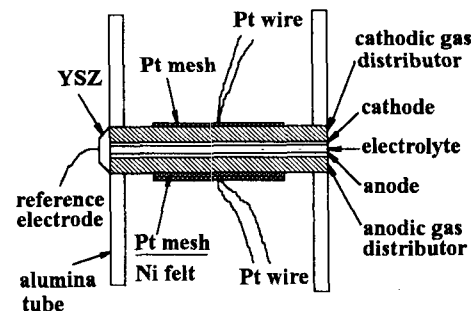


Fig.2 Schematic diagram of the experimental set-up for the electrochemical tests of the single cell with an area of 1.25 cm².

The single cells of 1.25 cm² were tested at 1000 °C. Figure 2 shows a schematic diagram of experimental set-up for the electrochemical tests of the single cell. 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 interruption and the ac impedance methods. The impedance was measured using impedance/gain analyzer (Solartron SI 1260) in the range of 0.1 to 10^5 Hz with dc bias.

Table 1 Effect of the applied pressure on the flattening treatment of the single cell.

Applied pressure (Pa)	Heating rate ($^{\circ}\text{C}/\text{h}$)	Comments
318	45	warped still
483	45	flattened partially
637	45	flattened
802	45	flattened
955	45	cracked partially
1273	45	cracked
637	68	cracked partially
1592*	68	flattened

* The samples processed at 318 or 483 Pa were treated again at this condition.

3 RESULTS AND DISCUSSION

3.1 Fabrication of the flat cell

In order to make a planar SOFC, it is required to obtain flat cell components. To avoid a warpage of cell components, the gas distributor 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 and gas distributors, and thus the flattening treatment was conducted. The results of flattening treatment for the single cells with an area of 83 cm^2 were summarized in Table 1. The flat cell components were obtained under pressures of 637 and 802 Pa at $1380\text{ }^{\circ}\text{C}$, 3 h with heating rate of $45\text{ }^{\circ}\text{C}/\text{h}$. From an observation of scanning electron microscope (SEM), it was confirmed that the interfaces of electrode/electrolyte and electrode/gas distributor were flat, and there were no crack and void along the interfaces. The gas distributor had a porous structure enough to supply reactant gases. 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.

3.2 Polarization characteristics of the co-fired cell

The performances of co-fired cells with an area of 1.25 cm^2 were measured after operation of 24 h at $1000\text{ }^{\circ}\text{C}$ and the result was shown in Fig.3. The maximum power in the co-fired cells of two layers and of three layers attained $200\text{ mW}/\text{cm}^2$ and 20

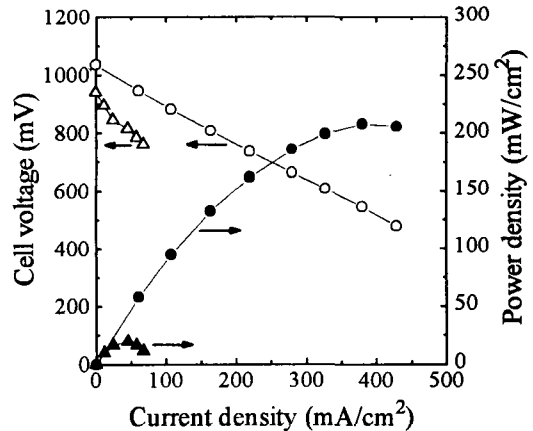


Fig.3 Performance of the co-fired cell of two layers (O, ●) and of three layers (Δ, ▲) after operation at $1000\text{ }^{\circ}\text{C}$, 24 h.

mW/cm^2 , respectively. The performance of three layers' cell was very low as compared to that of two layers' cell. To find reason of the cell performance loss, the electrode overvoltages and iR losses were evaluated by a current interruption method. The polarization characteristic features in the co-fired cells are illustrated in Figs.4 and 5.

In the co-fired cell of two layers, 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 6 shows an electrical conductivity of the anode gas distributor as a function of holding time, which was measured in hydrogen atmosphere at $1000\text{ }^{\circ}\text{C}$. 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.4 and 5. In contrast to that of two layers, a much larger iR drop

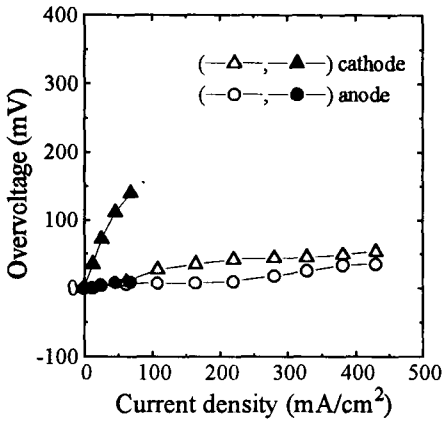


Fig.4 Comparison of electrode overvoltages in the co-fired cells of two layers (O, Δ) and three layers (●, ▲) after operation at 1000 °C, 24 h.

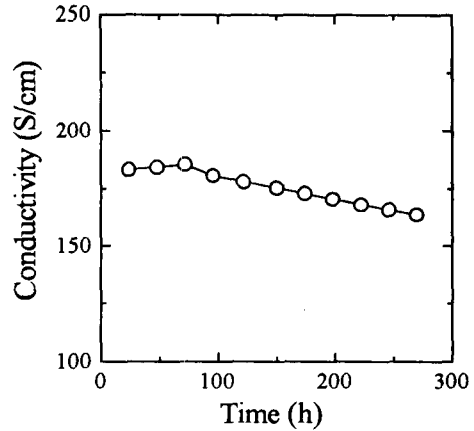


Fig.6 Electrical conductivity of the anodic gas distributor as a function of holding time. This was measured in H₂ at 1000 °C.

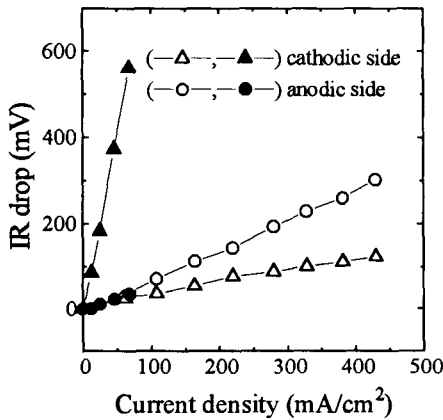


Fig.5 Comparison of iR drops in the co-fired cells of two layers (O, Δ) and three layers (●, ▲) after operation at 1000 °C, 24 h.

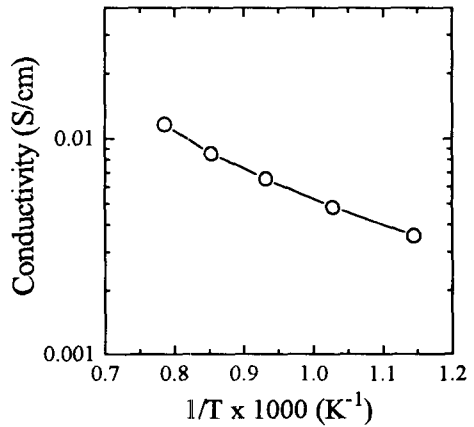


Fig.7 Electrical conductivity of the cathodic gas distributor measured in air.

existed in the cathodic side, which was found to be due to poor conductivity of the cathode gas distributor, as shown in Fig.7. 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.⁹⁾ This means loss of cathodic activity, that is, development of a large cathodic overvoltage.

3.3 Impedance behavior during the cell operation

In order to test the long term stability of the cells, the cell was kept under open circuit state at 1000 °C for 150 h. Figure 8 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 (open circuit state, at 1000°C). To evaluate the degradation factors, ac impedance was measured and the results were represented in Figs.9 and 10. The impedance plot indicates that the cell performance decay is due to the increases of both iR drop and electrode overvoltages.

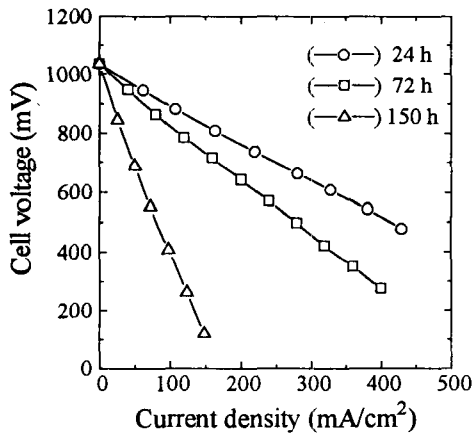


Fig.8 Performance of the co-fired cell of two layers as a function of operating time.

Most of iR drop came from the degradation of anodic side as shown in Fig.10, which is attributed to the poor contact of the anodic side because the anode and anodic gas distributor are considered to have still high conductivity. The poor contact may originate from the decrease of contact pressure between current collector and anode gas distributor, or the formation of microcracks at interfaces of anode side. To make clear its reason, the cross sections at the interfaces of anode/electrolyte and anode/anode gas distributor after operation of 24 and 150 h were examined using SEM. The microcracks were not observed at the interfaces. Thus the poor contact of the anodic side is considered to be due to the decrease of the contact pressure, which produces the increased contact resistance. 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.^{10,11)}

Figure 11 shows the impedance plot after operation of 150 h as a function of direct current. The internal resistance of the cell remained constant value irrespective of current density but the polarization resistance decreased with increasing current density. The polarization resistance is related to the reaction process of the electrode. Assuming that the electrodic reaction process in the planar electrode is valid in the porous electrode, the polarization curves at the activation-controlled region (η_{act}) and at the concentration-controlled region (η_{conc}) are described as a function of current density(i) by the following equations:

$$\eta_{act} = k_1 + k_2 \log i \quad (1)$$

$$\eta_{conc} = k_3 \log(1 - i/i_1) \quad (2)$$

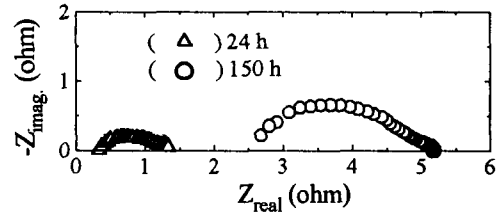


Fig.9 Impedance plot for the co-fired cell of two layers at two different operating times, which was measured at the direct current of 30 mA.

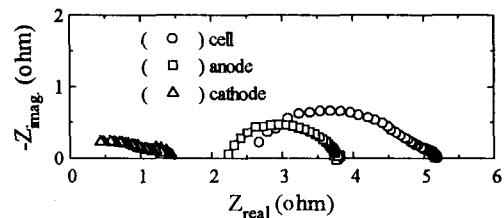


Fig.10 Impedance plot for the co-fired cell of two layers measured at the direct current of 30 mA after operation at 1000 °C, 150 h.

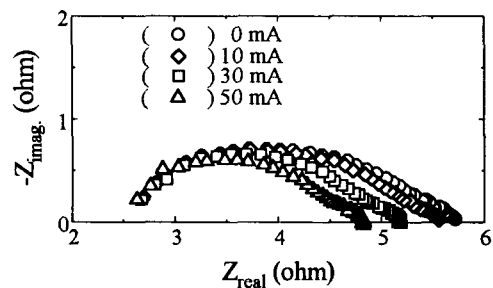


Fig.11 Impedance plot for the co-fired cell of two layers as a function of direct current after operation at 1000 °C, 150 h.

where k_i is constant which depends on temperature and charge transfer coefficient, and i_1 is a limiting current density. From eqs.(1) and (2), the polarization resistances at the activation region ($|d\eta_{act}/di|$) and at the concentration region($|d\eta_{conc}/di|$) are given by the following equations:

$$\left| \frac{d\eta_{act}}{di} \right| = \left| \frac{k_2}{i} \right| \quad (3)$$

$$\left| \frac{d\eta_{conc}}{di} \right| = \left| \frac{k_3}{(i_1 - i)} \right| \quad (4)$$

The above equations mean that when the electrode reaction obeys the activation process, the polarization resistance decreases with increasing current density, but in the case of concentration-controlled process the

polarization resistance increases with current density. Therefore by comparing the impedance data of Fig.11 with the above equations, the electrode reaction in the co-fired cell of two layers is considered to be controlled by the activation process within a current of 50 mA

3.4 Some problems in composite plate process

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) increase of contact resistance between anodic gas distributor and current collector during operation.
- (4) increase of overvoltage at anode during operation.

The instability of the anodic gas distributor arises from the degradation of its electrical conductivity. From Fig.6, the decay rate of the electrical conductivity in the anodic gas distributor is found to be 80 S/cm per 1000 h. Although its conductivity remains high within several hundred hours, it should be noted that the decay rate is rapid. The remarkable decrease of the electrical conductivity in the anodic gas distributor may be 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 anodic 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. The increase of Ni volume in the anodic gas distributor is remained for future work. Generally, the increase of contact resistance among the interconnector, the anodic gas distributor and the anode is 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 the increase 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.^{10,11} 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.

4 CONCLUSION

The composite plate process for fabricating the planar solid oxide fuel cell was investigated. A flat cell of 7.7×10.8 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.

(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) In the co-fired cell of two layers, the measured impedance results during the cell operation showed that the performance decay is due to the increases of both anode overvoltage and iR drop at anode side. Also the electrode reaction of the co-fired two layers' cell is considered to be controlled by the activation energy process within the low current of 50 mA.

(4) For future works, the improvement of electrical conductivity of gas distributors, especially the development of the cathodic gas distributor with high electronic conductivity is required.

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