

# Fabrication and Characterization of Anode Supported YSZ/GDC Bilayer Electrolyte SOFC Using Dry Press Process

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*In the present paper, we fabricated and tested anode-supported solid oxide fuelcell(SOFC) with gadolinium-doped(GDC) and yttria-stabilized zirconia (YSZ) electrolyte. The bilayer electrolyte thin film, consisting of a 8  $\mu\text{m}$  thick YSZ layer and a 40  $\mu\text{m}$  thick GDC layer, was prepared by a simple dry-pressing with simple spray coating process which is cost-effective method. The two electrolyte layers were sintered 1400°C together, and no crack and delamination at the interface were observed. An open-circuit voltage of 0.91 V and a maximum power density of over 218 mW/cm<sup>2</sup> were measured with 3% H<sub>2</sub>O-H<sub>2</sub> as fuel and air as oxidant at 600°C. The result shows that the electronic conductivity of GDC electrolyte was blocked by the thin YSZ electrolyte functional layer.*

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## 1. Introduction

The fact that hydrogen will be the last energy source became no more attractive to us. The main issue is which kind of energy conversion device will be going to survive in the future. Since many researchers highlighted the fuel cell as the next generation power source, a lot of researched have been conducted to commercialize it.

SOFCs have many advantages in comparison with typical PEMFCs which have shown water management problem, usage of novel catalyst, patent issue for polymer electrolyte, expansive graphite bipolar plate and CO poisoning. So many researchers in energy field have been thought SOFC would be the promising device.

But the main bottle neck for the commercialization of SOFC has been its high operation temperature. It can cause thermal mismatch between MEA, nickel agglomeration, reactions between component materials, restricted sealant choice and expensive inter-connector material. So we focused our interest to IT-SOFC. Its temperature position can avoid many problems of HTSOFC and LT-SOFC maintaining the competitiveness of original SOFC's characteristics.

Solid oxide fuel cells (SOFCs) are one of more promising technology for mobile and stationary applications. Decreasing the operating temperature of SOFCs from conventional to an intermediate temperature can offer many advantages. Low material temperature

degradation, high system reliability, and long stack life time can decrease interconnect materials and fabrication costs. Significant efforts have been achieved to lower the operating temperature of SOFCs.<sup>1-6</sup> Three methods have been adopted to reduce the electrolyte thickness that uses new electrolyte materials with high ionic conductivity at a lower temperature, and declining polarization resistance in an intermediate temperature. Doped ceria (CeO<sub>2</sub>), which has a much higher ionic conductivity at an intermediate temperature than the more popular electrolyte material of yttria-stabilized zirconia (YSZ), is regarded as one of the more hopeful candidates for the intermediate temperature SOFCs electrolyte.

Many researchers have reported various processes of fabrication for intermediate SOFCs based on a thin-film electrolyte doped ceria such as tape casting,<sup>7</sup> screen printing,<sup>8,9</sup> dry pressing,<sup>10,11</sup> spray coating,<sup>12,13</sup> spin coating,<sup>3</sup> slurry coating,<sup>14</sup> sol-gel<sup>15</sup> and alternative processes.<sup>22,23</sup> However, the reduction of ceria from Ce<sup>4+</sup> to Ce<sup>3+</sup> in a reducing atmosphere will increase electronic conductivity, which decreases the open-circuit voltage (OCV) of the cell. Furthermore, reduction of ceria also causes lattice expansion of the ceria electrolyte at the anode side. One approach proposed to prevent the OCV drop and to improve the chemical and mechanical stability of doped ceria electrolytes in reducing atmospheres is to coat thin YSZ film on the anode side of a doped ceria electrolyte. The YSZ/GDC bilayer electrolyte can be a

barrier of a doped ceria electrolyte from a reducing mood.

Since the ionic conductivity of YSZ is lower than gadolinia-doped ceria (GDC) at an intermediate temperature, the YSZ film as an electronic and hydrogen blocking layer should be adequately thin to minimize its contribution to total electrolyte resistance. Therefore, techniques such as chemical vapor deposition (CVD),<sup>16</sup> pulsed laser deposition (PLD),<sup>17,21</sup> RF magnetron sputtering,<sup>18</sup> and wet-ceramic process<sup>19</sup> have been developed to deposit a thin film of YSZ on doped ceria electrolyte.

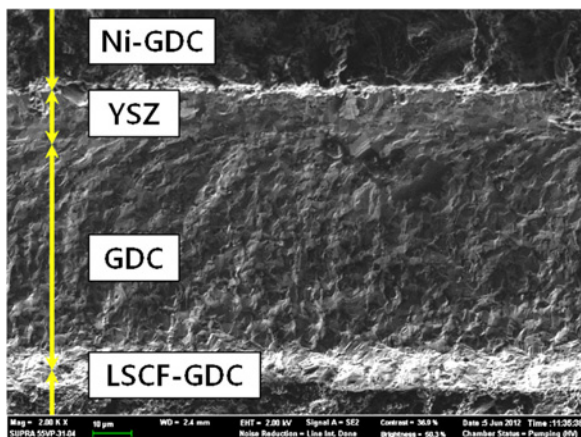
In this paper, we develop a simple, rapid and cost-effective method, which is based on dry pressing and powder spray coating process. The spray dry co-pressing method is developed to prepare a dense bilayer electrolyte thin film for anode-supported SOFCs. The dry pressing method is a simple, reproducible, and very cost effective process. This technique has been widely used in the laboratory and industry to produce a thick substrate. However, it is very difficult to prepare a thin electrolyte by the dry pressing method because of the difficulty in controlling the uniform distribution of electrolyte powder on a substrate surface. Consequently, the powder spray coating process is employed in this study. The powder spray process is a simple and cost-effective method with a thickness of less than 10  $\mu\text{m}$ .

In the following sections, we describe the process of spray dry co-pressing and we prepare a dense YSZ/GDC electrolyte films on porous nickel oxide (NiO)-GDC substrates. We also measure and discuss the

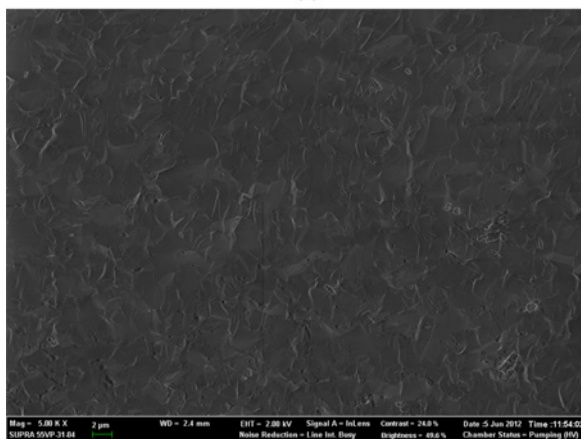
electrochemical performance of an anode supported SOFC with an YSZ/GDC electrolyte thin film prepared by the spray dry co-pressing process.

## 2. Research Methodology

GDC ( $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ , Nextech, USA) and 8mol% YSZ ( $\text{Y}_2\text{O}_3/\text{ZrO}_2$ , Nextech, USA) commercial powders were used as an electrolyte. Commercial NiO (60 wt %) and GDC (40 wt %) powder were mixed and ground with alcohol and a little amount of polyvinyl butyral (PVB) for two hours. Afterward, the mixture was dried and screened through a 110-mesh sieve. For the preparation of the green body, the NiO and GDC mixed powder was first pressed under 60 MPa into a substrate in a SKD11 steel die. Then, the YSZ slurry was mixed properly with isopropanol and was spray coated onto a NiO/GDC substrate that is in steel die. Finally, the GDC powder was added onto the YSZ layer through a sieve and co-pressed at 80 MPa to form a green assembly. The green assembly was subsequently co-fired at 1400°C for five hours in air. A dense, crack-free and well-bonded GDC-YSZ bilayer electrolyte-anode assembly was obtained.

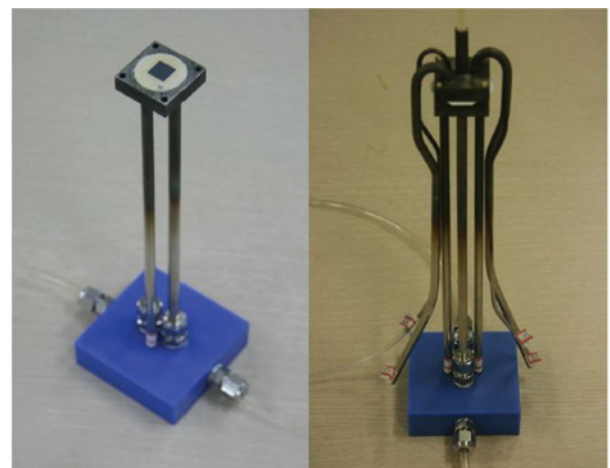


(a)

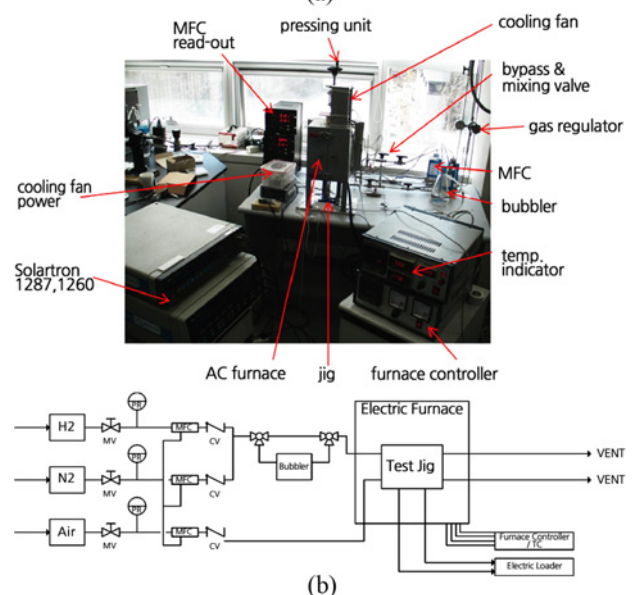


(b)

Fig. 1 (a) Scanning electron microscopy of cross-section of a YSZ/GDC bilayer electrolyte film on a anode substrate (b) a morphology of GDC electrolyte plane



(a)



(b)

Fig. 2 (a) button cell supporting fixture design for experiments (b) Button cell test station and P&ID diagram

The diameters of the green pellets and sintered pellets were 25 and 22 mm, respectively. The thickness of the YSZ and GDC layers was controlled by the spray time and amount of powder, respectively. The total thickness of the electrolyte-anode substrate assembly was 2 mm. The porous cathode was prepared using a mixture of 60 wt% strontium-doped lanthanum cobaltite ferrite ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ) and 40 wt% GDC. The mixture was applied by screen printing and was fired at 900°C for two hours in air. The area of the cathode was 0.5 cm<sup>2</sup>.

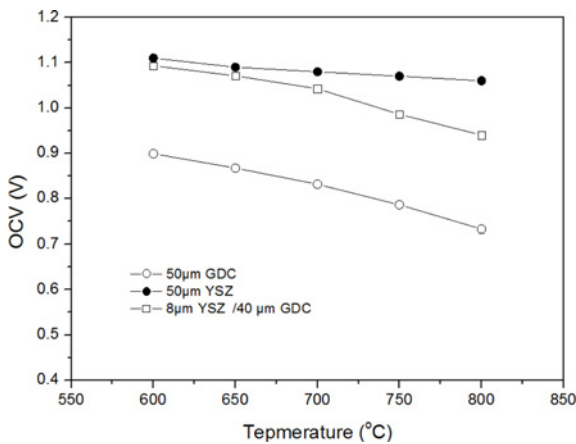


Fig. 3 Measured OCV vs temperature for single cells with 50 μm GDC monolayer electrolyte, 50 μm YSZ monolayer electrolyte, and 8 μm YSZ/ 40 μm GDC bilayer electrolyte, respectively

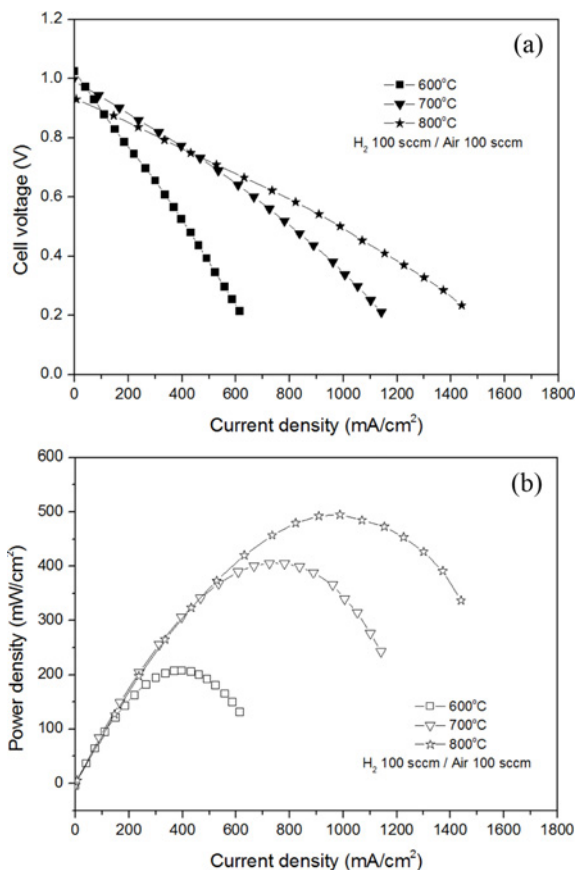


Fig. 4 (a) Cell voltage and (b) power density as function of current density of a YSZ (8 μm)/GDC (40 μm) bilayer electrolyte cell measured between 600 and 800°C in humidified hydrogen and open air

Fig. 2(a) shows button cell supporting fixture design for experiments. The single cell was sealed using a gold ring on one end of an INCONEL jig. The surface of outer side of gold ring was coated ceramic sealant (Aremco 503) to prevent leakage of hydrogen. Platinum meshes were used as current collectors. The single cell was pressured by a bolt of jig. After the in situ reduction of the NiO anode in H<sub>2</sub> for several hours, the performances of the cell were measured at various temperatures from 600 to 800°C. Hydrogen passed over the anode at a flow rate of 100 sccm with 3% H<sub>2</sub>O, and air flowed over the cathode surface at a flow rate of 100 sccm. The impedances were measured typically in the frequency range from 0.05 Hz to 50 kHz under open-circuit conditions using a Solartron 1287 potentiostat and 1260 frequency-response analyzer. Fig. 2(b) shows whole button cell test station and P&ID diagram. The tested cell was fractured and examined by a scanning electron microscopy (SEM). The SEM observation was performed on a scanning electron microscope (SUPRA 55VP, Carl Zeiss).

### 3. Results

The YSZ layer is required to be dense and crack-free to prevent exposure of the GDC layer to the hydrogen. This effectively serves as an electronic blocking layer. In addition, the YSZ film is required to be suitably thin to minimize the ohmic resistance of the electrolyte. Figs. 1(a) and 1(b) show cross-sectional and surface micrographs of the YSZ/GDC bilayer electrolyte film on a reduced Ni-YSZ anode substrate. Total thickness of the YSZ/GDC bilayer electrolyte is about 50 μm, which consists of a 8 μm YSZ layer and a 40 μm GDC layer.

In addition, a uniform film YSZ is joined well by a NiO-GDC anode substrate. The YSZ film is also densely sintered without any cracks and pores. Finally, the GDC film is well bonded to the LSCF cathode. This SEM measurement was measured for several hours after the electrochemical operations. This suggests that the cell by dry co-pressing process verifies that the YSZ/GDC bonding is very stable even under the operation of the fuel cell. It also indicates that the two electrolyte layers and anode layer are thermo-mechanically matched during the high temperature co-sintering process. The interfacial diffusion during the high-temperature co-sintering (1100°C~) that

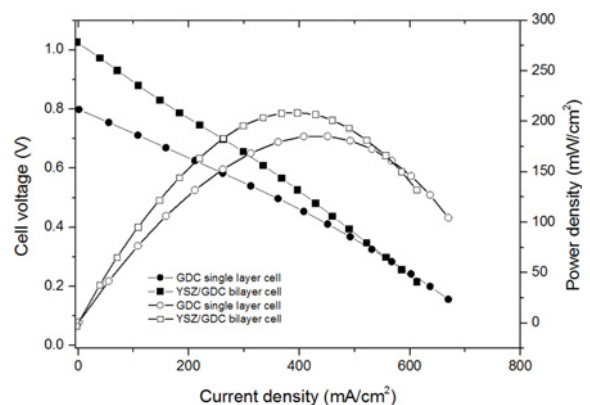


Fig. 5 Cell voltage and power density vs. current density of YSZ (8 μm)/GDC (40 μm) bilayer electrolyte cell measured 600°C in humidified hydrogen and open air

causes the formation of solid solutions at the interface of YSZ and GDC layers. Zhou et al.<sup>20</sup> investigated the thermal expansion behavior of  $(\text{GDC})_x(\text{YSZ})_{1-x}$  solid solutions in detail and found that the TEC of the  $(\text{GDC})_x(\text{YSZ})_{1-x}$  system increases with increasing GDC fraction from that of pure YSZ ( $\sim 10.7 \times 10^{-6} \text{ K}^{-1}$ ) to that of pure GDC ( $\sim 13.2 \times 10^{-6} \text{ K}^{-1}$ ). This behavior implies that the formation of solid solutions from YSZ/GDC diffusion interface will create a functional graded layer between the YSZ and GDC layers, which would help to reduce the thermo-mechanical breakdown of a fuel cell with the YSZ/GDC bilayer electrolyte.

The  $(\text{GDC})_x(\text{YSZ})_{1-x}$  layer has low ionic conductivity which increase ohmic overvoltage, but it has positive effect to mechanical stability and open circuit voltage. So, total performance is improved.

With respect to the YSZ/GDC bilayer electrolyte cell by dry co-pressing quality, a GDC single electrolyte cell and YSZ single electrolyte cell were prepared using a LSCF-GDC (50:50 by weight) composite material as the cathode. Subsequently, the single electrolyte cells were electrochemically tested in humidified hydrogen (3 vol.%  $\text{H}_2\text{O}$ )/air (20%  $\text{O}_2$ ; 80%  $\text{N}_2$ ) at a temperature range of 600 to 800°C. The electrolyte thickness for both single cells was about 50  $\mu\text{m}$ , and thus, the same electrolyte thickness of the total YSZ/GDC bilayer cell. Fig. 3 shows the measurement of the OCVs of the GDC single layer cell, YSZ single layer cell, and the YSZ/GDC bilayer cell. The OCVs of the YSZ/GDC bilayer cell is 1.09, 1.07, 1.042, 0.98 and 0.94 V at 600, 650, 700, 750, and 800°C, respectively. The OCVs of the YSZ/GDC is more enhanced than the OCVs of the GDC single layer cell. However, it is lower than the OCVs of the YSZ single cell at high temperature range. It is considered that sealing issues or YSZ micro-crack affects decrease of OCVs results. In this reason, we regards that the YSZ layer in the YSZ/GDC bilayer cell prevents reduction of the GDC electrolyte.

The current-power density and current-voltage characteristics of the YSZ/GDC bilayer electrolyte cell were measured between 600 to 800°C. Fig. 4(b) shows that the maximum power densities of the YSZ/GDC bilayer electrolyte cell are 208, 403, 481  $\text{mW}/\text{cm}^2$  at the temperatures of 600, 700, and 800°C, respectively. For the purpose of comparison, the current-power density and current-voltage characteristics of the GDC single layer cell was measured in the same manner. Fig. 5 shows the characteristics measurement of the GDC

single layer electrolyte cell and YSZ/GDC bilayer electrolyte cell at 600°C. The maximum power density of the GDC single layer cell is 180  $\text{mW}/\text{cm}^2$ . The result demonstrates that the peak performance of the YSZ/GDC bilayer cell is higher than one of the GDC single cells because of higher OCVs. Fig. 6 shows an electrochemical impedance spectroscopy (EIS) result regarding the GDC single electrolyte cell and YSZ/GDC bilayer electrolyte cell. Actually, assuming both of electrolytes have same thickness, YSZ/GDC electrolyte should have higher ohmic potential than GDC single layer electrolyte, because of YSZ electrolyte layer has lower ionic conductivity than GDC electrolyte in intermediate temperature. However, in this study, the YSZ/GDC bilayer electrolyte cell has lower ohmic resistance than one of the GDC single layer electrolyte cells. It means that the YSZ film layer in the YSZ/GDC electrolyte prevents reduction of the ceria electrolyte, even though the YSZ film has low ionic conductivity in an intermediate temperature. It is considered that reduced GDC electrolyte cell has poor contact properties between electrolyte surface and anode surface. Thus, the results demonstrate that the micron thickness of the YSZ film is sufficiently effective.

#### 4. Conclusions

The spray dry co-pressing method was developed as a simple, rapid and cost-effective method. An anode-supported SOFC single cell with YSZ-GDC bilayer electrolytes, Ni-GDC cermet as an anode, and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF)-GDC composite as a cathode was fabricated. The SOFCs based on YSZ-GDC bilayer electrolytes were tested from 600 to 800°C with hydrogen, which contained 3% water as fuel and air as an oxidant. Maximum power densities of 218 and 421  $\text{mW}/\text{cm}^2$  were achieved at 600 and 800°C, respectively. The OCV was 0.91 and 0.68 V at 600 and 800°C, respectively. The results suggest that the spray dry co-pressing technique is a practical process to prepare bilayered dense electrolyte films for low-temperature SOFC applications. In addition, the findings suggest that for a thin-film cell with YSZ/GDC bilayer electrolytes, the reactions between YSZ and cathode material at high temperatures can be prevented. However, the electronic conductivity of a GDC electrolyte is blocked by the YSZ layer.

Future study will be focused on decreasing sintering temperature. Reduced sintering temperature can prevent reaction between YSZ and GDC which has negative effect to ionic conductivity. Many researchers are studying another material added to the electrolyte to lower the sintering temperature. We can prevent the disadvantage of YSZ-GDC solution by combining these studies.

In addition, in this study, we did not employ sufficiently porous anode substrate which can offer low concentration and activation overvoltage. So, we will employ anode pore-former for increasing power density, in future study.

In this study, we employed about 10  $\mu\text{m}$  YSZ functional layer for reproducibility. The 10  $\mu\text{m}$  YSZ layer could be considered thick for functional layer. But if we would set the spray step and compaction step automatically, the functional YSZ layer will be controlled about 1~2  $\mu\text{m}$ . And then, we will get the enhanced performance and characteristic.

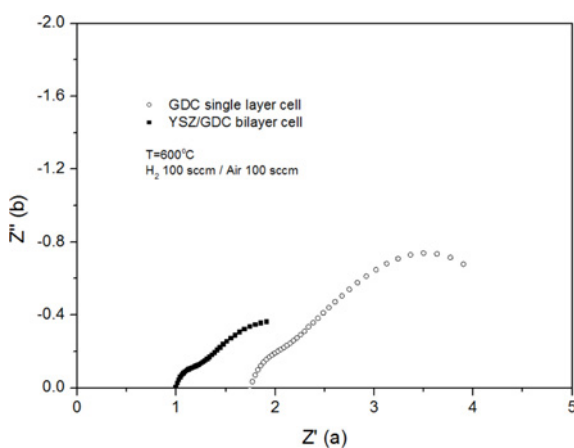


Fig. 6 Result of electrochemical impedance spectroscopy of GDC single electrolyte cell and YSZ/GDC bilayer electrolyte cell, 600°C

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