High Current Density of Solid Oxide Fuel Cell with Anode Support via Phase Inversion Method

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ABSTRACT

Anode support is prepared using phase inversion method and directly used for anode supported solid oxide fuel cell. The anode substrate is about 560 µm in thickness and has a porosity of 60.0%. The finger-like pore layer is 522 µm in thickness, in which the finger-like pore diameter is about 30 µm. The sponge layer is 28 µm in thickness and has a porosity of 46.1%. The single cell with Ni-YSZ/YSZ/GDC/BaCo0.4Fe0.4Zr0.1Y0.1O3-δ configuration is fabricated with YSZ electrolyte on the skin layer. At 800°C and under an output voltage of 0.64 V, the single cell attains a power density of 3.33 W cm⁻². At 700°C, 750°C and 800°C, the single cell outputs a current density over 5.2 A cm⁻² without the appearance of limited current density from gas transport. The results depict gas transport in the anode substrate with the sponge layer and the skin layer is highly efficient.

Keywords : Solid Oxide Fuel Cell, Phase Inversion, High Current Density

1. Introduction

Anode-supported solid oxide fuel cells (SOFCs) have attracted increasing attention due to their high power density, low operating temperature, reduced ohmic loss as well as low fabrication cost.⁴⁻⁶ The anodes directly prepared by traditional dry-pressing and tape-casting techniques are generally larger than 0.7 mm in thickness and have a low porosity of about 0.3 and small pore size of less than 0.5 µm, which are not efficient in gas transport and lead to the appearance of limited current density.⁶ In order to facilitate gas transport, pore formers such as graphite and starch are introduced into the green tape and then burn out during the sintering process to increase porosity and pore size in anodes. Suzuki fabricated an anode supported tubular cell having a power density of greater than 1 W cm⁻² at 600°C using PMMA as a pore former.⁷ Haslam fabricated an anode using 20 wt% rice starch as a pore former and got a single cell with the maximum power density of over 1.2 W cm⁻².⁸ Shimada prepared an anode with a porosity of 0.54 and a pore diameter of 0.91 µm by adding a mixture of graphite carbon and cellulose as a pore former and obtained a single cell with the maximum power density of 3.09 W cm⁻² at 800°C.⁹ These works well depict the importance and tortuous pore paths produced by these pore formers, mass transport is still governed by Knudsen diffusion and ordinary diffusion simultaneously.¹⁰,¹¹ The further increase in porosity can lead to severe losses in the mechanical strength and electrical conductivity of anode.⁹

Recently, phase inversion method was applied to the fabricating of anode for SOFCs.¹²,¹³ The anode prepared via phase inversion has a three-layer structure including skin layer, finger-like pore interlayer and sponge bottom layer.¹⁴ The finger-like pores with diameter tens of microns provide fast tracks for gas transport. The skin layer or sponge layer was regarded as a barrier for gas transport and removed in some researches.¹⁵ Huang developed a co-tape casting method for anode and graphite, and removed the sponge layer of graphite through calcination in air.¹⁶ The limited current density did not appear on the cell at a high current density of 3 A cm⁻².¹⁷ Dong removed the skin layer with the assistant of stainless steel mesh, but the cell only produced the maximum power density of 772 mW cm⁻².¹⁸ The skin layer or sponge layer can also be removed by acids erosion or by laser ablation technique.¹⁹ The removing processes are complex and increase fabrication cost. Some work also reported single cells without the removal of the skin layer or sponge layer, but the single cells exhibited low power density and current density.¹⁶ Therefore, the low current density and power density without the appearance of limited current density on these cells cannot depict whether it is necessary to remove the skin layer or the sponge layer.

In the anode prepared using phase inversion method, the sponge layer or the skin layer is less than one tenth of the anode thickness and has a relatively high porosity. The hindrance of the sponge layer to gas transport in anode can be so small that limited current density cannot appear at a very high current density. In order to verify this point, we fabricated anode-supported SOFC with anode prepared using phase-inversion method without removal of the sponge layer or the skin layer. In order to attain a high current density, a thin electrolyte film to reduce ohmic resistance and a high oxygen reaction activity cathode of BaCo0.4Fe0.4Zr0.1Y0.1O3-δ (BCFZY) to reduce polarization resistance were integrated into the cell. We characterized the anode substrate and the single cell and measured the electrochemical performance of the single cell.

2. Experimental

3.86 wt% Polysulphone (PSF) and 0.94 wt% polyvinylpyrrolidone (PVP) were dissolved in 23.2 wt% 1-methyl-2-pyrrolidone (NMP) to form a homogeneous organic solution. 72 wt% powder mixture of NiO and yttria-stabilized zirconia (YSZ) weight ratio of 6:4 were added into the solution and ball milled for 24 h. The anode slurry was tape casted into a 750 µm thick layer on a glass plate and then
immersed into water bath at room temperature for solidification. To get an anode sample with complete sponge structure, one tape-casted sample was solidified in air for more than 30 min. The obtained green NiO-YSZ tapes were cut into discs with a diameter of 25 mm and dried at 60°C in air. The dried green discs were pre-sintered at 1200°C for 2 h. The YSZ electrolyte film was coated on the skin layer side of pre-sintered anode discs and sintered at 1300°C in air for 7 h. To prevent the reaction between YSZ and cathode, a gadolinia-doped ceria (GDC) barrier layer was prepared on YSZ film by reactive magnetron sputtering method.12 BCFZY cathode was coated on the surface of GDC film and sintered at 900°C for 2 h. The effective cathode area was 0.5 cm². For the measurement of porosity, the green anode discs and the green tapes with a complete sponge structure were also sintered at 1300°C for 7 h and then reduced in hydrogen at 800°C for 1 h.

The microscopy photos of the anode and the cell were taken on a scanning electron microscope (SEM, JSM-7800F). The anode porosity was measured by Archimedes method in water. The electrochemical performance was tested on a home-made cell evaluation device. Nickel mesh on the anode side and golden mesh on the cathode side were used as current collectors. Two nickel wires connected to the Ni mesh and two Au wires connected to the Au mesh were used to collect current and voltage of anode and cathode, respectively. The single cell was sealed to two alurnina tubes and supplied with humidified hydrogen flow (3 mol% H₂O, 100 ml min⁻¹) as fuel and oxygen flow (100 ml min⁻¹) as oxidant. The AC impedance spectra under open circuit voltage conditions were measured on an electrochemical workstation (Solartron 1260 impedance analyzer combined with Solartron 1287 electrochemical interface) in the frequency ranging from 10⁶ to 0.08 Hz and with 10 mV signal amplitude.

### 3. Results and Discussion

Figure 1 shows the structure of the anode substrate fabricated by phase inversion method and after pre-sintered at 1200°C. The anode substrate depicts a typical three-layer structure as previous reported,14 including skin layer, finger-like pore interlayer and sponge bottom layer. It is depicted in Fig. 1 that the finger-like pores have much larger pore diameter at the sponge layer side than that at the skin layer side, indicating that it is good for gas transport and electrochemical reaction to select the skin layer as the anode function layer. Besides, many cracks are observed in the area between the finger-like pore layer and the sponge layer. There are some related works summarized in Table 1, where the skin layer or sponge layer is selected as the anode function layer for varied reasons.16,17,20,22,23 But the selections are all for the benefit of gas transport or electrochemical reaction. Thus, considered from either gas transport or the structure stability of cell according to the structure, it is better to select the skin layer to support the electrolyte film here.

Figure 2 shows the cross-sectional SEM images of the single cell. The anode is about 560 µm in thickness and remains the three-layer structure after reduction (Fig. 2a). The porosity of the reduced anode measured by Archimedes method is 60.0%. For comparison, the porosity of the anode substrate reported by other researchers is summarized in Table 2. The porosity for the anode reported in this paper is lower than those of previously reported anodes which can be due to the higher solid loading of NiO and YSZ powders during the phase inversion process and the presence of lower porosity of sponge layer and skin layer in this work.20,22,24 The skin layer is about 10 µm in thickness and has a porous structure (Fig. 2b). In the skin layer, Ni particles and YSZ particles are well contacted, which provide large TPBs for electrochemical oxidation of fuels. The skin layer also is well connected with the YSZ film. The finger-like pore layer is 522 µm in thickness and occupies about 93% anode thickness. The finger-like pores distribute in anode uniformly. The pore diameter increases from several micrometers in the top part, to about 30 µm in the middle and then to about 70 µm in the bottom part. As these pore diameters are much larger than the molecular mean free paths of H₂O and H₂, it can be expected that ordinary diffusion is responsible for gas transport in these finger-like pores. The thickness of pore wall is about several micrometers in the top part but in the bottom part it is from about 20 µm to about 30 µm. The relatively low porosity in pore walls can lead to good connections of Ni particles, which results in high electrical conductivity. The sponge layer is 28 µm in thickness, which occupies about 5% of the total anode thickness (Fig. 2c). The porosity of the reduced sponge layer is 46.1%, larger than that of the traditional anode substrate.25 The low thickness and high porosity of the sponge layer indicate a lower hindrance for gas transport. The cross-sectional SEM image in Fig. 2d shows a good connection of the YSZ film, GDC layer and cathode. Both the YSZ film and GDC interlayer have a dense structure. The thicknesses of the YSZ film, GDC interlayer and BCFZY cathode are 4 µm, 300 nm and 17 µm, respectively. Thus, the single cell is well constructed for high current density solid oxide fuel cell.

![Figure 1.](image)

**Table 1.** The layer selected as anode function layer.

| Selected layer | Reason | Ref |
|----------------|--------|-----|
| Skin layer     | The sponger layer was much thicker and hindered fuel transport. | 16 |
| Sponger layer  | The thickness of the sponger layer was easy to control by adjusting the blade gap. | 22 |
| Sponge layer   | The porosity of the skin layer was lower and might limit the gas diffusion. | 17, 23 |
| Sponger layer  | The sponge layer provided more active reaction sites. | 20 |

The I-V and I-P curves of the cell at temperatures from 650 to 800°C are given in Fig. 3. The OCVs of the single cell at 650, 700, 750°C and 800°C are 1.16 V, 1.15, 1.14 and 1.13 V, respectively, well in agreement with the theoretical values calculated by the Nernst equation of 1.16, 1.15, 1.14 and 1.14 V, respectively. At 800°C and under an output voltage of 0.64 V, the single cell attains a power density of 3.33 W cm⁻². Besides, the power densities under an output voltage of 0.75 V are 1.52, 1.99, 2.42 and 2.77 W cm⁻² at 650, 700, 750 and 800°C, respectively. The output current density
attains 5.16 A cm\(^{-2}\) at 0.53 V and 700°C, 5.28 A cm\(^{-2}\) at 0.59 V and 750°C and 5.22 A cm\(^{-2}\) at 0.64 V and 800°C. Even if the current density exceeds 5.2 A cm\(^{-2}\) and the fuel utilization exceeds 19.4% under these conditions, the convex-up curvatures from the limited current densities are not observed in the I-V curves. The conventional anode supported cells reached limited current density at 3.6 A cm\(^{-2}\) and 2.5 A cm\(^{-2}\) from inefficient gas transport in anodes.\(^5,8\) The much higher current density of over 5.2 A cm\(^{-2}\) and much higher power density of 3.33 W cm\(^{-2}\) without the presence of limited current density in this work well depict that the anode with the sponge layer and the skin layer is highly efficient in gas transport. On the one hand, the gas transport in the anode can be the highly efficient in gas transport in the finger-like pore layer through ordinary diffusion, which is different from the gas transport govern by both Knudsen diffusion and ordinary diffusion in the conventional anode. Though the gas transport in the spongy layer is govern by both Knudsen diffusion and ordinary diffusion, the thin sponge layer, only occupying 5% of the total anode thickness, with higher porosity of 46.1% than most of the conventional anodes, makes its resistance to gas transport greatly reduced. The high current density over 5.2 A cm\(^{-2}\) without the presence of limited current density depicts that the removal of the spongy layer is not an important issue.

The electrochemical impedance spectra (EIS) of the single cell under open circuit voltage are shown in Fig. 4a. The first intersection at high frequency represents the ohm resistance \(R_o\), the second intersection at low frequency represents the total resistance \(R_t\) and the difference between \(R_t\) and \(R_o\) is the polarization resistance \(R_p\). The \(R_o\) increases from 0.18 Ω cm\(^{-2}\) to 0.49 Ω cm\(^{-2}\), the \(R_p\) increased from 0.09 Ω cm\(^{-2}\) to 0.12 Ω cm\(^{-2}\), and \(R_p\) increased from 0.09 Ω cm\(^{-2}\) to 0.37 Ω cm\(^{-2}\) as the temperature decreased from 800°C to 650°C. The \(R_p\) is larger than the calculated
ohm resistance (~0.01 Ω cm²) of electrolyte according to the known conductivities of YSZ film and GDC interlayer combined with their thicknesses, and this may originate from the contact resistance caused by the mismatch of the thermal expansion coefficients between GDC and BCFZY cathode.26,27 Thus, the performance of the single cell can be further enhanced by optimizing the cathode in the future.

The equivalent circuit shown in Fig. 4b is built to fit the impedance arcs. R₁, R₂ and R₃ correspond to the high-, mid-, and low frequency arcs, respectively. R₁ and R₂ are the activation polarization resistances of the anode and cathode, and R₃ is caused by the concentration polarization of anode and cathode including gas transport and surface diffusions.9 The fitting curve at each temperature is shown in Fig. 4c, Fig. 4d, Fig. 4e, and Fig. 4f, respectively. And the fitted values are shown in Table 3. As the temperature decreases from 800°C to 650°C, R₃ slightly increases from 0.067 Ω cm² to 0.084 Ω cm². For comparison, the concentration polarization resistances of single cells with anode substrate prepared

**Table 3.** Resistances from the fitting EIS data of the single cell.

| Temperature (°C) | Rₑ (Ω cm²) | R₁ (Ω cm²) | R₂ (Ω cm²) | R₃ (Ω cm²) | Rₑ (Ω cm²) |
|-----------------|------------|------------|------------|------------|------------|
| 800             | 0.077      | 0.035      | 0.006      | 0.067      | 0.108      |
| 750             | 0.081      | 0.059      | 0.029      | 0.072      | 0.160      |
| 700             | 0.093      | 0.062      | 0.095      | 0.076      | 0.233      |
| 650             | 0.114      | 0.076      | 0.216      | 0.084      | 0.376      |

Figure 4. Impedance spectra on the anode-supported single cell under OCV conditions (a), the equivalent circuit model built to fit the impedance spectra (b), and the fitting curves at 800°C (c), 750°C (d), 700°C (e), and 600°C (f).
via different method are summarized in Table 4. R3 in this work is similar to that of the anode supported SOFC prepared through phase inversion in the previous work and much smaller than that of the traditional anode supported SOFC.24,28,29 The results of the equivalent circuit indicate that the anode substrate prepared by phase inversion method facilitates the gas transport efficiently and it is unnecessary to remove the sponge layer.

4. Conclusions

A single cell with Ni-YSZ/YSZ/GDC/BCFZY configuration was fabricated with anode substrate prepared via phase inversion method. The anode substrate was 560 µm in thickness and had a porosity of 60.0%. The finger-like pore layer was 522 µm in thickness and the pore diameter was 30 µm. The sponge layer was 28 µm in thickness and had a porosity of 46.1%. At 800°C, the power density under an output voltage of 0.64 V was 3.33 W cm⁻² at 700°C, 750°C and 800°C, the single cell outputted a current density under an output voltage of 0.64 V was 3.33 W cm⁻² 28 µm in thickness and had a porosity of 46.1

Table 4. The concentration polarization resistances of single cell with different anode substrate.

| Preparing method | Temperature (°C) | Concentration polarization resistances (Ω cm²) | Ref |
|------------------|------------------|-----------------------------------------------|-----|
| Tape casting     | 800              | 0.496                                         |     |
| Dry pressing     | 600              | 0.265                                         |     |
| Phase inversion  | 700              | 0.090                                         |     |
| Phase inversion  | 700              | 0.076                                         |     |
|                  |                  |                                               | This work |

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