Fabrication and characterization of the anode-supported solid oxide fuel cell with Ni current collector layer

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The anode-supported solid oxide fuel cell (SOFC) is constructed by a screen-printed double-layer cathode, an air-tight yttria-stabilized zirconia (YSZ) as electrolyte, and a porous Ni-YSZ as anode substrate. A thin Ni film is fabricated as an anode current collector layer to improve the performance of the SOFC. The operation parameters are systematically investigated, such as feed rates of the reactants, operation temperature, contact pressure between current collectors and unit cell on the cell performance. The SEM results show that the YSZ thin film is fully dense with a thickness of 8 μm and exhibits the good compatibility between cathode and electrolyte layers. The maximum power density of the cell with Ni current collector layer is 366 mW cm^{-2} at 800°C. This value is approximately 1.3 times higher than that of the cell without Ni layer. According to the electrochemical results, the Ni current collector layer decreases the ohmic and polarization resistances. The contact pressure results between cell and test housing show that cell performance efficiency is enhanced at the high current density region.

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1. Introduction

The solid oxide fuel cells (SOFCs) are electrochemical devices which directly convert the chemical energy of the applied fuel to electricity and therefore have been considered as the highly efficient and environmentally friendly energy-conversion system. The advantages of SOFC are high efficiency for energy conversion, low polluting emissions, and high selectivity of fuel sources. Yttria-stabilized zirconia (YSZ) and strontium-doped lanthanum manganite (LSM) have been extensively used as the electrolyte and cathode for SOFC,⁽¹⁻⁴⁾ respectively. It is well recognized that YSZ has high oxygen ionic conductivity, good mechanical properties and LSM has high electronic conductivity. The thermal expansion coefficient and the chemical stability of LSM are in good compatibility with YSZ.⁽⁴⁾ However, high operating temperature at 800°C is required for conventional SOFC to achieve low overall resistance of the cell which is favorable for performance behavior.

The reduction of cell resistance for performance enhancement has been widely reported.^(3,5-7) The approaches to alleviate the ohmic loss of the cell include reduction of electrolyte thickness,⁽³⁾ selection of alternative electrolyte materials with higher ionic conductivity [such as gadolinia-doped ceria (GDC)],^(6,7) and decrease of the contact resistance between the current collectors and electrodes. According to prior reports, the contact resistance has a significant effect on the electrochemical performance.^(4,8) Therefore, the reduction of the interface resistance between the current collectors and electrodes is an effective method for performance enhancement. Two approaches are used to reduce the contact resistance. One is to increase the contact pressure between the current collector and electrode. The ohmic resistance

decreases accordingly with the contact pressure. The other is to add a Ni layer as the anode current collector layer on the surface of anode substrate, increasing the electronic conductivity and catalytic activities as well. This Ni layer is expected to enhance the electrochemical performance and reduce the interfacial resistance between the current collector and anode electrode. The increase of the contact pressure can decrease the ohmic resistance of the current pickup from the cell, thus enhancing the overall cell performance.^(4,8)

In this study, the anode-supported SOFC with structure of Ni||Ni-YSZ||YSZ||GDC-LSM||LSM was fabricated. The effect of Ni layer as the current collector on electrochemical performance was investigated. The operational variables of the cell performance, such as operation temperature, feed rates of gas reactants, and contact pressure between the current collectors and electrodes have been investigated in the influence on the polarization behavior. The microstructure, electrochemical performance, and AC-impedance analysis of the cell were also concerned and reported in this study.

2. Experimental

2.1 Fabrication of the single cell

An anode-supported solid oxide fuel cell with structure of Ni (anode current collector layer) || Ni-YSZ (anode) || YSZ (electrolyte) || LSM-GDC (functional layer) || LSM (cathode) was fabricated with a cathode active area of approximately 16 cm^2 . The anode substrate and the Ni current collector layer were prepared via tape casting process and sintered at 1400°C for 4 h. The casting was performed using a tape casting system (ECS, Model CS-8) of laboratory model. The YSZ electrolyte was made onto the anode substrate via spin coating method and sintered at 1400°C for 4 h. The GDC-LSM paste (Fuelcellmaterials com., FCM) was printed onto the YSZ electrolyte layer as the cathode functional layer (CFL) and LSM paste (Fuelcellmaterials com.,

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FCM) was printed onto the CFL as cathode current collector layer (CCCL) using a screen printer and then sintered at 1150°C for 3 h.

2.2 Characterizations of materials and cell

The morphology of the cross-sections of the single cell was observed via field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). The composition of the single cell was analyzed by energy dispersive X-ray spectrometer (EDX, Horiba, 7539H). The cell was set in an in-house constructed measurement station for the investigation of the electrochemical property. The cell performance was measured at different operating temperatures with the inlet fuel/oxidant of pure H₂ or H₂+N₂ mixture/air. The flow rates of H₂ and air were 335 and 670 ml min⁻¹, respectively. AC impedance measurements were performed using an impedance analyzer (Solartron 1260) under an open circuit condition with frequency from 10 KHz to 0.01 Hz.

3. Results and discussion

3.1 Microstructure of the cell

SEM micrographs of the cross section of the Ni/Ni-YSZ//YSZ//LSM-GDC/LSM cell structure are shown in **Fig. 1**. It clearly shows that the YSZ electrolyte layer has dense structure with a thickness of approximately 8 μm and exhibits the well interfacial contacts with both Ni-YSZ anode and LSM-GDC cathode functional layers. This indicates that it is feasible to prepare a thin YSZ electrolyte layer by spin coating onto the anode substrate. Both the composite cathode layers and anode substrate have the porous microstructures to assure good diffusion for gas reactants. **Figure 2** presents the SEM images of the LSM-GDC/LSM composite cathode layers, YSZ-Ni/Ni composite anode layers, and their elemental distributions, obtained with the linear scanning analysis using EDX. The thicknesses of the LSM-GDC cathode functional layer and Ni current collector layer are about 14 μm [see Fig. 2(A)] and 32 μm [see Fig. 2(B)], respectively. The total thickness of the cathode layer is approximately 56 μm, consisting of ~14 μm LSM-GDC layer and ~42

μm LSM layer. **Figure 3** shows the micrographs of the cross section of the cell without a Ni current collector layer. It shows that the microstructures of both cells are similar except for the part of the anode current collector (see Figs. 1 and 2).

3.2 Cell performance and polarization analysis

The scheme of the detailed structure of the cell test housing is shown in **Fig. 4**. In **Fig. 5**, the long-term performance test of the unit cell was operated for about 189 h. The open-circuit voltage (OCV) of the cell is higher than 1.0 V that indicates the existence of an airtight structure of the YSZ electrolyte. Until 100th hours, the OCV shows a slightly drop due to the adjustment of the cell test system. The *I*-*V* curves and power densities with different hydrogen concentrations in the fuel feed are shown in **Fig. 6(a)**. It shows that the maximum power density increased with the

Fig. 1. SEM micrographs of the cross section of the anode-supported cell with a thickness of 8 μm for YSZ electrolyte.

Fig. 2. EDX analysis of (a) the LSM-GDC/LSM composite cathode layers and (b) the Ni/Ni-YSZ composite anode layers with the linear scanning analysis of elements.

Fig. 3. SEM micrographs of the cross section of the anode-supported cell without a Ni layer as anode functional layer.

Fig. 4. The scheme of the detailed structure of the cell test housing.

increase of the hydrogen concentration from 114.4 to 139.2 mW cm^{-2} under constant feed rate (335 ml min^{-1}) at 700°C . These I - V curves are nearly identical with the different hydrogen concentrations at low current density region (activation region). At high current density region (ohmic/diffusion polarization region), the current density and the cell performance are enhanced by the increase of hydrogen concentrations at the fixed cell voltage. This indicates that the increase of hydrogen concentration improves the diffusion polarization at anode and has no influence on the electrode kinetics. Figure 6(b) shows the effect of hydrogen concentration on the polarization behavior of the cell at 700°C . In Fig. 6(b), the impedance spectra consist of two semi-circles indicating that at least two different electrode processes were exhibited in correspondence with the high- and low-frequency arcs during the electrochemical reaction of the cell. According to the prior reports,^{5),7),9)} the high frequency arc can be attributed to the migration of oxygen ions from electrode to the electrolyte and the low frequency arc can be attributed to the oxygen reduction processes. Several steps of mechanism are involved in the oxygen reduction process, including oxygen transfer, dissociative adsorption, and the surface diffusion of the oxygen intermediate species on the electrode.^{5),9)} In high-

Fig. 5. The process of the cell performance test for 189 h.

Fig. 6. Effect of hydrogen concentration on: (a) performance and (b) polarization behavior of the unit cell at 700°C (Flow rate of air = 335 ml min^{-1}).

frequency range, the impedance spectra are almost invariant with the different hydrogen concentration. In low-frequency range, the impedance obviously increased with the decrease of the hydrogen concentration. This suggests that the increased impedance can be attributed to the hydrogen diffusion limitation in the anode layer.⁷⁾ According to the above results, the high hydrogen concentration improves the mass transfer in anode and has no influence on charge transfer of the cell.

The cell performance tests were executed at operation temperature ranged from 700 to 800°C and the results of I - V and I - P curves were presented in Fig. 7(a). The maximum power densities are 139.2, 228.1, and 366.4 mW cm^{-2} at the temperatures of

Fig. 7. (a) Cell performance and (b) impedance spectra of the unit cell measured at different operating temperatures.

700, 750, and 800 °C with reactants of H_2 and air at the flow rates of 335 and 670 $ml\ min^{-1}$, respectively. The performance of the single cell was increased with the increasing of operating temperature. The OCV values of the cell are constantly higher than 1.0 V, which indicates that no gas leakage occurred through the YSZ electrolyte layer of the cell and no crack is existed on YSZ film during the performance test. This argument is in agreement with the result of SEM observation. Figure 7(b) shows the cell impedance spectra at different operating temperatures. The total electrode polarization resistance and ohmic resistance are estimated from the impedance spectra. The high frequency intercept corresponds to the ohmic resistance (R_E) including electrolyte, electrodes and the connection wire resistances. The low frequency intercept corresponds to the total resistance (R_{total}) of the cell. Therefore, the resistance between the high frequency and low frequency intercepts with real axis represents the polarization resistance (R_p) of the cell.^{10),11)} All kinds of resistance decrease with the increasing temperature which indicates that the oxygen ion transfer on YSZ electrolyte film and the electrochemical reaction process are promoted by the increase of temperature. Further, Fig. 8 shows the total cell resistance, polarization resistance, and ohmic resistance of the cell. At 700, 750, and 800 °C, the ohmic resistances are 0.45, 0.34, and 0.3 $\Omega\ cm^2$; and the polarization resistances are 4.89, 3.04, and 1.43 $\Omega\ cm^2$, respectively. The decreased ohmic resistance is due to the increase of operating temperature which leads to high migration rate of oxygen ion in the electrolyte film. Within the electrodes, the increase of the operating temperature promotes the electrochemical reaction at TPB sites as well.^{4),5)} This effect can lead to the decrease of the polarization resistance at elevated temperature. The ratio of R_p to R_t increases progressively with the decreasing temperature, from 0.83 at 800 °C to 0.92 at 700 °C, respectively. It indicates that the total resistance ($R_E + R_p$) of the unit cell is

Fig. 8. The ohmic resistance (R_E), polarization resistance (R_p), and total resistance (R_t) determined from the impedance spectra of the unit cell at different operating temperatures and the ratio of R_p to R_t is also shown in this figure.

Fig. 9. Effect of Ni anode current collector layer on (a) performance and (b) impedance behavior of the unit cell at 800 °C.

mainly governed by the polarization resistance, and the effect of electrode polarization on the total cell resistance ($R_E + R_p$) decreases with the increase of the operating temperature.

Figure 9 shows the effect of Ni current collector layer on the performance and impedance behaviors at 800 °C. In Fig. 9(a), it shows the peak power density of the cell with and without Ni current collector layer are 366.4 and 289.5 $mW\ cm^{-2}$, respectively. In contrast, the peak power density of the cell with a Ni current collector layer, which is approximately 1.3 times higher than that of the cell without a Ni current collector layer. In Fig. 9(b), the ohmic and polarization resistances of the cell with a Ni current collector are lower than those of the case without a Ni current collector layer. The decreased resistance ($R_E + R_p$) may be attributed to the Ni current collector layer which reduces the

Fig. 10. Effect of contact pressure between current collector and electrodes on the cell performance measured at 800°C.

interfacial resistance and polarization resistance between the current collector and anode electrode. According to the above results, the Ni current collector layer can improve the electrochemical reaction and reduce the ohmic resistance. The combinative effects result in a sharp enhancement of the cell performance. It is consistent with the reported contents by Wang et al.¹²⁾ due to the elimination of Ni depleted layer in this regard. However, the peak power density and fuel utilization of the cell are limited due to the low porosity of the anode substrate used in this study.

3.3 The influences of the contact pressure between current collector and MEA on the cell performance

The cell performance tests were executed by applying different contact pressures to the system of MEA-current collector at 800°C and the results are shown in Fig. 10. From the I - V curves, the apparent cell resistance decreases and the maximum power density increases from 354.3 to 396.2 mW cm⁻² with increasing contact pressure from 12.3 to 42.9 KPa. At low current density (activity region), the variation of I - V plots is not prominent under various contact pressures. At high current density (ohmic polarization region), the effect of the weight load on the cell performance is obvious. This indicates that the increase of contact pressure improves ohmic resistance of the cell and has no influence on the electrode kinetics. This result is in agreement with the prior reports.^{4),5),8)} Hence, the decrease of resistance can be attributed to the ohmic part of the cell. The ohmic resistance is determined by the electrolyte of the cell, current collector, and the circuit of the measurement system. The ohmic resistances of the circuit of the measurement system and electrolyte of the cell are assumed to be no impact under the various contact pressures. The contribution of the decrease of the ohmic resistance is mainly governed by current pickup of the cell. According to the above discussion, the electrical conductivity should be affected by the contact pressure applied to the current collector of test housing on the cell. This means that the electrical conductivity between the cell and the measurement system influences the overall cell performance significantly.

4. Conclusions

The effect of operation conditions on performance of an anode-supported SOFC (Ni/Ni-YSZ//YSZ//LSM-GDC/LSM) has been investigated. The I - V characteristics show a significant role

of the hydrogen concentration, which indicates that the high hydrogen concentration improves the mass transfer in anode and has no influence on the charge transfer of the cell. From the performance test of the cell, the maximum power densities obtained are 139.2, 228.1, and 366.4 mW cm⁻² at 700, 750, and 800°C, respectively. The performance of the cell is enhanced and the total resistance of the cell is decreased with the increase of the operating temperature. Those results of performance test are in good agreement with the results of AC impedance analysis. The ohmic resistances (R_E) are 0.45, 0.34, and 0.30 Ω cm²; and the polarization resistances (R_p) are 4.89, 3.04, and 1.43 Ω cm² at 700, 750, and 800°C, respectively. The AC impedance analysis reveals that the total resistance of the cell is primarily limited by polarization resistance in the temperature range of 700–800°C.

The Ni current collector layer improved the performance of the cell, which showed approximately 1.3 times higher than that case without Ni current collector layer. However, it is important to improve the electrode structure to upgrade the cell performance. The contact pressure between the cell and the cell test housing must be kept high enough to enhance the overall cell performance. The maximum power density increases from 354.3 to 396.2 mW cm⁻² with the increase of contact pressure from 12.3 to 42.9 KPa. At low current density (reaction region), the variation of V - I plots is not prominent under various weight loads. At high current density (ohmic polarization region), the effect of the weight load on the cell performance is essentially obvious. This result indicates that the unit cell with a Ni current collector layer is recommended for enhancement of the cell performance. Both of the optimum contact pressure between electrodes and current collector of the stack¹³⁾ and the existence of a current collector layer adopted in the unit cell itself are critical issues for enhancement of the cell and stack performances.

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