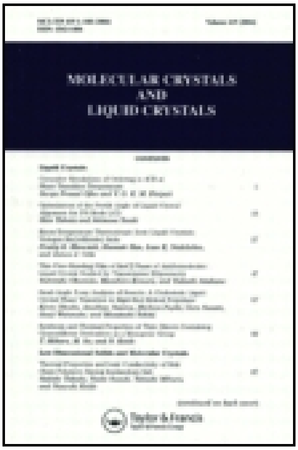

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Electrochemical Performance of Anode Supported Single Cells of Solid Oxide Fuel Cell with Anode/Electrolyte and Cathode/Electrolyte Interlayers

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Single cells of solid oxide fuel cell(SOFC) with thin film composite interlayers were fabricated in order to improve charge transfer reaction in the electrode/electrolyte interface. Yttria-stabilized zirconia(YSZ) slurry was prepared by mixing YSZ powder with typical organic dispersants, and the optimum YSZ slurry composition for the interlayer dip-coating was determined by employing backscattering flux measurements. By the insertion of interlayer, a denser YSZ electrolyte layer could be prepared and the electrochemical performance of SOFC could be enhanced significantly.

Keywords: composite; electrical properties; interlayer; organic dispersant; solid oxide fuel cells (SOFC)

INTRODUCTION

Solid oxide fuel cells (SOFCs) are considered one of the most important future power generation devices which can directly and efficiently convert chemical energy to electrical energy [1–5]. SOFCs have attracted a great attention due to their great fuel tolerance, high efficiency, and wide range of power generation applications. Electricity is generated through the reduction of oxygen to O^{-2} ions at the cathode, transfer of the anions through a solid electrolyte, yttria-stablilized zirconia

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(YSZ), and oxidation of the fuel with O^{-2} ions at the anode. One of the main obstacles in using SOFCs is their high operating temperature, which is around 900–1000°C. The high operating temperature limits the constructing materials for interconnections, current collectors, and sealants. Several attempts have been made to lower the operating temperature of SOFCs by using thin film electrolytes. Though thin film electrolyte enables to lower the operating temperature of SOFCs, drawbacks such as activation polarization are prevalent. Recently, application of thin film composite interlayers is introduced as a means to improve charge transfer reaction in the electrode/electrolyte interface. Although there have been a few reports on the benefit of using interlayer in SOFC, further studies are required to understand the effect of interlayers on the SOFC performances.

In this study, anode-supported SOFC single cells with electrode interlayer were fabricated and the effect of interlayer on the cell performance was evaluated. Colloidal slurries of YSZ have been prepared by mixing YSZ powder, binder, solvent, and dispersants, and their dispersion stability was studied. The electrochemical performances of SOFC single cells were evaluated by polarization curves and impedance spectra in the temperature range between 700 and 900°C, using humidified hydrogen as fuel and air as oxidant.

EXPERIMENTAL

Preparation of Electrolyte and Interlayer Slurry

2 g of PVB (polyvinylbutyral, binder) and 2 g of DBP (dibutylphtalate, plasticizer) were dissolved in the solvent mixture of 28 g of toluene and 47.2 g of 2-propanol. 20 g of YSZ(Tosoh), and 0.4 g of fish oil (Sigma, dispersant) were added in the solution, and ball milled at 106.85 rpm for 24 hours to prepare YSZ electrolyte slurry. Terpineol (Fluka) was used instead of fish oil to compare as a dispersant. Anode/electrolyte interlayer slurry was prepared using the same composition of YSZ slurry except that 10 g of NiO was added instead of 10 g of YSZ. Cathode/electrolyte slurry was prepared using 10 g of LSM (strontium-doped lanthanum manganite) instead of NiO. The dispersion properties of the slurry were measured using TURBISCAN (Turbiscan Lab Expert, Formulaction).

Cell Fabrication

18 g of YSZ and 44.4 g of nickel acetate (Fluka, 99%) were mixed in 250 ml ethanol (99.9%) and heated on hot plate under vigorous stirring to evaporate the ethanol, and was fired at 450°C to prepare YSZ-NiO powder.

The mixture of the powder, PVB (binder), and carbon black (pore former) was ball milled for 24 h and then pressed to form disk pellets with the diameter of 1.5 cm and height of 2 mm. The pellets were pre-sintered in air at 1300°C to prepare Ni-YSZ anode support. Colloidal slurries of anode/electrolyte interlayer, electrolyte, and cathode/electrolyte interlayer were dip-coated (IPAE) onto the anode support and dried at 350°C subsequently and sintered at 1400°C for 5 h. Cathode paste was prepared by mixing 10 g of YSZ, 10 g of LSM, 0.1 g of PVB in 6 mL of terpineol and screen printed onto the cathode-electrolyte interlayer, and was sintered at 1200°C for 3 h. Pt paste was painted onto the anode and cathode of cell with an area of 0.5 cm^2.

Microstructure and Electrochemical Analysis

The cell was mounted in a cell tester (Probo Stat, NorECS) and electrochemical analysis was performed using frequency response analyzer (Solartron 1255B) coupled to a Electrochemical Interface (Solartron 1287) in the rage of 0.1 Hz $\sim$ 1 MHz with amplitude signal of 100 mV. Pt wires were connected to Pt meshes connected to LSM cathode current collector and the Ni-YSZ anode support current collector, and were used for current collection and voltage measurement. The cell was heated to 500°C in N_2 ambient and to 700°C in mixture of 5% H_2 + 95% N_2 on the anode side. At 700°C, the pure H_2 was circulated past the anode for 2 h to reduce NiO from the anode to Ni. After the anode reduction, humidified hydrogen was circulated past the anode and air was circulated past the cathode side. The voltage drop vs. current density and impedance spectra were obtained at the temperature range of 700–900°C. The cells were fractured and the microstructure of the cells was analyzed by scanning electron microscope (SEM, Hitachi S-4700).

RESULT AND DISCUSSION

The Dispersion Stability of YSZ Slurry

The dispersion properties of YSZ slurry was measured using TURBISCAN. This apparatus allows the investigation of the dispersion stability and homogeneity of the mixtures via periodical turbidity scan over sample height. The glass cell containing YSZ slurry was placed in the apparatus and its flocculation behavior was monitored every 30 min for 24 h. The backscattering intensity vs. height data were collected. By tracing the change of primary backscattering intensity, the dispersion stability can be measured. YSZ slurry was prepared by using fish oil and terpineol as a dispersant. Figure 1(a) shows the turbidity scan over fish oil driven

YSZ sample cell height, and Figure 1(b) shows delta backscattering flux of both samples. Figure 1(a) shows that YSZ slurry is well dispersed at the beginning, but its dispersion gradually becomes poor. Figure 1(b) shows that YSZ slurry with fish oil as a dispersant is more stable than that with terpineol. The dispersion stability is dependent on the long-chain molecules adsorbed onto the particle surface and is achieved when the repulsive forces are high enough to overcome the attractive Van der Waal's forces. Fish oil contains palmitic acid and stearic acid which have long-chained carboxylic acid, and forces the hydrocarbon chain to remain in the solvent

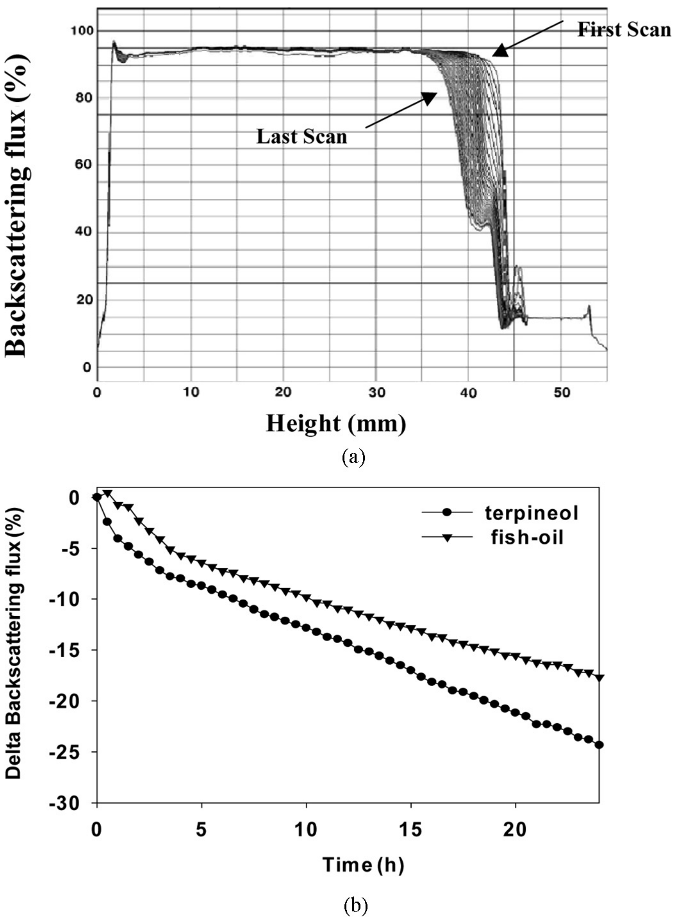


FIGURE 1 (a) Back scattering scan over YSZ- fish oil cell height and (b) time dependent delta backscattering of YSZ slurry.

adjacent to the particles surface and so provides steric stabilization. These long chains can make chelate complexes with the YSZ particles surface and adsorb strongly to the YSZ particles in the suspension [6]. In the case of terpineol, it appears that the hydroxide group adsorbed poorly to the YSZ particles.

Microstructure Analysis

SEM micrographs of the fracture surface of single cells after testing are shown in Figure 2. The figure shows that the electrolyte layer without interlayer has more pores and cracks compared to electrolytes with interlayer. It is speculated that slurry driven anode interlayer is denser than palletized anode, and this affect the porosity of YSZ electrolyte layer. More dense crystal growth in electrolyte layer can be expected with dense interlayer surface than that with porous anode support. Interlayer also can balance the thermal expansion

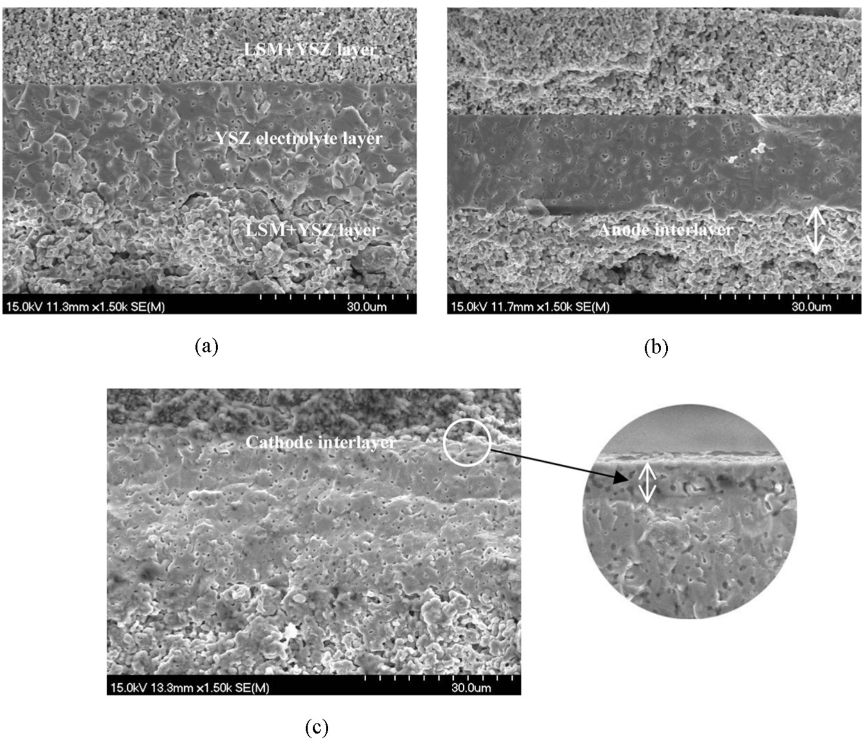


FIGURE 2 SEM micrograph of cross-section of SOFC. (a) SOFC without interlayer, (b) SOFC with anode interlayer, and (c) SOFC with cathode interlayer.

discrepancy of electrolyte layer and electrode. When the electrode and electrolyte were sintered together without interlayer, stress will be accumulated in the interface due to the different thermal expansion coefficients of NiO (anode material), LSM (cathode material), and YSZ (electrolyte material), and this induces the growth of ohmic resistance. By the addition of the anode interlayer, the unbalanced thermal expansion of two phases can be relieved.

Electrochemical Performance

The results of electrochemical impedance spectrum analysis carried out at 700 ~ 900°C are shown in Figure 3. In the figure, two semicircular features are observed from low frequency to high frequency. In addition, as the operating temperature increases from 700 to 900°C,

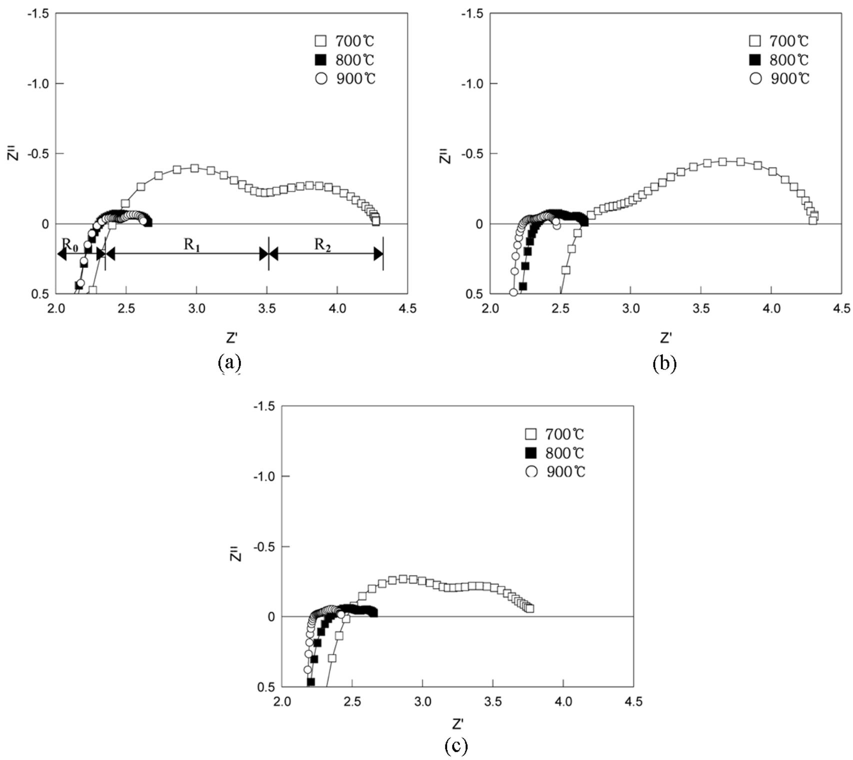
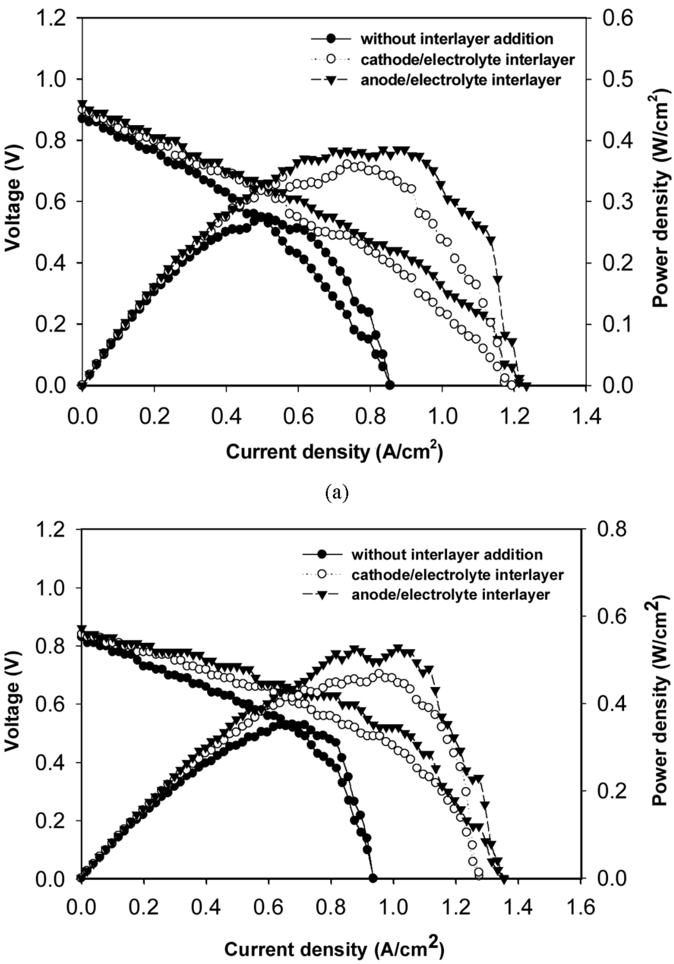


FIGURE 3 Electrochemical impedance spectroscopy diagrams of the SOFC. (a) SOFC without interlayer, (b) SOFC with cathode interlayer, and (c) SOFC with anode interlayer.

the area specific resistance decreases. This can be attributed to the increase of ionic conductivity of electrolyte and rate of electrochemical reactions with the increase of temperature [7]. The figure also shows a high frequency intercept (R_0) which is related to the electrolyte resistance, platinum wire resistance, and current collector resistance. At intermediary and low frequency ranges, two semicircular resistances expressed as R_1 and R_2 are observed. R_1 at intermediary frequency



(b)

FIGURE 4 I–V and power density curves of SOFCs measured at (a) 800 and (b) 900°C.

range indicates electrode/electrolyte interfacial resistance and R_2 at low frequency range indicates electrochemical reaction resistance taking place at the electrodes. And the value of $R_1 + R_2$ represents polarization resistances (R_p) in the single cell. At 700°C, R_1 and R_2 values without interlayer were 1.167 and 1.103 Ω (current collector area = 0.5 cm^2), with cathode interlayer were 0.555 and 1.45 Ω;, and with anode interlayer were 0.902 and 0.92 Ω;, respectively. The polarization resistances (R_p) for each cell decrease from 2.27, 2 and 1.82 Ω; at 700°C to 0.373, 0.311, and 0.262 Ω; at 900°C. This shows that polarization resistance can be decreased either by increase of operating temperature or by the insertion of electrode/electrolyte interfacial layer. This may be attributed to the improvement of the charge transfer reaction in the electrode/electrolyte interface.

Figure 4 shows I–V and power density curves of SOFC at 800 and 900°C. The figure shows that the main voltage drop is related to the ohmic polarization of electrodes and electrolyte [8]. The open circuit voltage was 0.92 ~ 0.95 V at 700°C, 0.87 ~ 0.92 V at 800°C, 0.83 ~ 0.86 V at 900°C. The maximum power density (MPD) of single cell without interlayer, with cathode interlayer, and with anode interlayer at 800 were 0.273, 0.357, and 0.3854 W/cm^2, respectively. The corresponding values at 900°C were 0.352, 0.468, and 0.528 W/cm^2 at 900°C. The figure also shows that addition of anode interlayer improves the cell performance better than the addition of cathode interlayer. By the addition of electrode/electrolyte interlayer in SOFC, the ion transmission area of the interface can be significantly expanded accelerating the charge-transfer reaction at the interface, and electrochemical performance can be enhanced.

CONCLUSIONS

The optimum YSZ slurry components for the interlayer dip-coating could be determined by employing backscattering flux measurements and the fish-oil additive was more effective than terpineol for YSZ slurry stabilization. By the insertion of interlayers, denser YSZ electrolyte layer could be prepared. Moreover, by the addition of electrode/electrolyte interlayers in SOFC, the ion transmission area of the interface can be significantly expanded, and electrochemical performance was enhanced by 30%.

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