

Short communication

## Effects of anode and electrolyte microstructures on performance of solid oxide fuel cells

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### Abstract

To improve the performance of anode-supported solid oxide fuel cells (SOFCs), various types of single cells are manufactured using a thin-film electrolyte of Yttria stabilized zirconia (YSZ) and an anode functional layer composed of a NiO–YSZ nano-composite powder. Microstructural/electrochemical analyses are conducted. Single-cell performances are highly dependent on electrolyte thickness, to the degree that the maximum power density increases from 0.74 to 1.12 W cm<sup>-2</sup> according to a decrease in electrolyte thickness from 10.5 to 6.5 μm at 800 °C. The anode functional layer reduced the polarization resistance of a single cell from 1.07 to 0.48 Ω cm<sup>2</sup> at 800 °C. This is attributed to the provision by the anode layer of a highly reactive and uniform electrode microstructure. It is concluded that optimization of the thickness and homogeneity of component microstructure improves single-cell performances.

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### 1. Introduction

With ever-increasing concerns about the environment and energy security, there comes even greater demand for the development of advanced technologies for electric power generation. The primary aims of such technologies are to eliminate emissions and to improve efficiency, thereby reducing the growing need to import and use fossil fuels [1–3]. Solid oxide fuel cells (SOFCs) provide many advantages over traditional energy conversion systems, namely, high efficiency, modularity, and low levels of NO<sub>x</sub> and SO<sub>x</sub> emissions [4]. Furthermore, because of the high temperature operation (800–1000 °C) of the SOFC, natural gas fuel can be reformed within the cell stack and thereby eliminates the need for an expensive, external reforming system. Nevertheless, costs and other technical challenges, including performance and durability, have prohibited entrance into mainstream power markets.

In the field of SOFC research, anode-supported designs have been extensively studied in recent years. They exhibit high power density, are mechanically strong, are relatively easy to scale-up, and allow for a reduction of the operating temperature. In order to improve the SOFC efficiency, each component should be optimized in terms of thickness and microstructure. From this point of view, the most practical and suitable approach for manufacturing the anode substrate for anode-supported SOFCs is the tape-casting process. Furthermore, it is potentially cost-effective for mass production.

In previous works [5,6], an effective anode microstructure was developed by using a NiO–YSZ composite powder, which was composed of nano-sized NiO and Yttria stabilized zirconia (YSZ) fixed on a YSZ core powder. The powder provides the electrodes with high reactivity, uniformity, and stability. Briefly, results showed that the performance and durability of single cells were highly improved by introducing the composite powder due to the uniform microstructure, increased three-phase boundaries (TPBs), and the constrained junction between NiO and YSZ. Nevertheless, the NiO–YSZ composite powder is unsuitable for use as a tape-casting material due to its high specific surface-area (>23.5 m<sup>2</sup> g<sup>-1</sup>). Therefore, it is reasonable to expect that a

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composite powder could be used as a functional layer material by a dip-coating process on an anode substrate made by tape-casting.

This work provides a discussion of technologies for manufacturing anode-supported SOFCs. In order to increase the performance and efficiency of a single cell, each component should be optimized in terms of the electrolyte thickness and the anode microstructure. Therefore, the relationship between the characteristics of the cell components and the single-cell performances is also discussed.

## 2. Experimental

### 2.1. Preparation of single cells

A porous NiO–YSZ anode support was fabricated by a tape-casting process. Toluene- and ethanol-based ceramic slurries containing a dispersant (M1201, Ferro, USA) and carbon black (Raven 430, Columbian Chemical, USA) as a pore former were milled for 24 h with zirconia balls. The ceramic materials were NiO (nickelous oxide green, J.T. Baker, USA), coarse YSZ (FTY 13.0-101H, Unitec Ceramics, UK), and fine YSZ (TZ-8Y, Tosoh, Japan) in a composition of 60 vol.% Ni–YSZ. The pre-milled slurries were ball-milled again with a commercial binder solution (B74001, Ferro, USA) for 24 h to produce slurries for tape-casting. Green anode sheets were formed by means of laboratory-scale tape-casting equipment. The green anodes were pre-sintered at 1300 °C to produce anode supports.

The above anode supports were dip-coated in NiO–YSZ slurries to produce anode functional layers. The dipping and drawing speed were 300 and 50 mm per min, respectively. Each sample was held at the bottom of the slurry for 25 s. The purpose of the functional layers is to aid electrolyte sintering by surface modification of the anode supports and to provide a large distribution of TPBs at the anode|electrolyte interface. The slurry for surface modification was prepared using NiO–YSZ composite powder (40 vol.% Ni–YSZ) developed in previous work [5,6]. A composite powder comprised of nano-sized NiO and YSZ fixed on a YSZ powder was prepared by the Pechini process. The particle size and the surface-area of the composite powder are 0.42  $\mu\text{m}$  and 23.55  $\text{m}^2 \text{g}^{-1}$ , respectively. The anode supports with a functional layer were pre-sintered at 1300 °C for 3 h.

The anode-supported electrolyte layers were fabricated by dip-coating YSZ slurry (viscosity 4.6 cP, solid loading 2.7%) on to a modified anode support. The Ni–YSZ anode support was then coated with YSZ sol (viscosity 3.5 cP, solid loading 0.42%) [7]. The particle-size distributions of the YSZ slurry and sol are shown in Fig. 1. Each coating solution exhibits a normal size distribution. The mean diameter of the YSZ particles of the slurry and the sol were 340 and 10 nm, respectively. The particle size of the YSZ sol is small enough to infiltrate pin-holes of the electrolyte layer, which is synthesized by YSZ slurry coating. Therefore, gas diffusion through the electrolyte layer could be obtained through a slight increase in the electrolyte thickness by a sol–gel coating process. The dipping and drawing speed were 300 and 50  $\text{mm min}^{-1}$ , respectively, and the dwelling time was

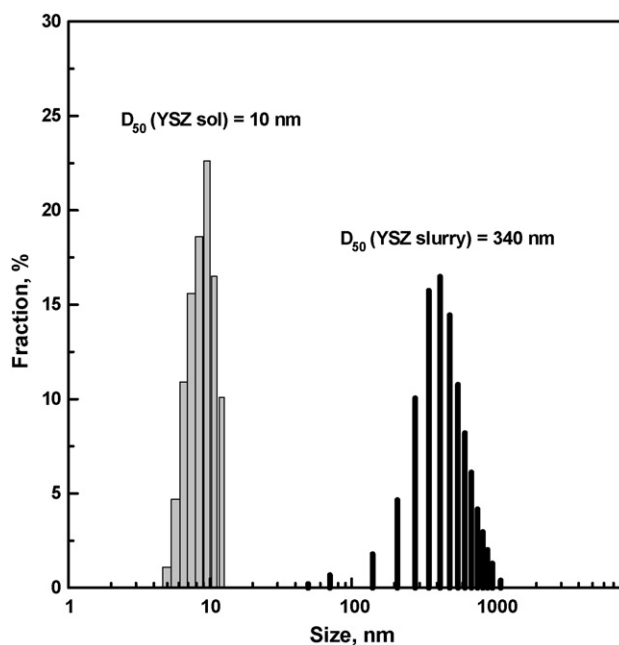


Fig. 1. Particle-size distributions of YSZ slurry and YSZ sol.

25 s. Each coated layer was dried at 300 °C for 1 h and sintered at 1400 °C for 3 h.

The cathode was fabricated by screen-printing with paste materials comprised of a mixture of powders and additives dispersed in an organic solvent prepared with a three-roll mill (EXAKT 35).  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (Praxair, USA) and YSZ (TZ-8YS, Tosoh) were used as cathode materials with a weight ratio of 50:50. The binder and solvent for the paste were ethylcellulose and  $\alpha$ -terpineol, respectively. The cathode paste was successively applied on the anode-supported electrolyte with an active area of 1.5  $\text{cm}^2$  and a thickness of 30  $\mu\text{m}$ . The cathode layer was sintered at 1150 °C for 3 h.

### 2.2. Single-cell tests

The 4-probe, single-cell test equipment was composed of spring-loaded alumina tubes to improve the gas sealing of the Pyrex O-ring (33  $\text{\O}_{\text{inner}}$ , 29  $\text{\O}_{\text{outer}}$ ) and the electrical contact between the electrodes and the current-collectors. The current-collectors were platinum mesh (Alfa, 52 mesh, 0.1 mm wire) and Ni felt for the cathode and the anode side, respectively. Platinum wires were used for all current-collectors and voltage leads.

The current–voltage characterization and durability were measured with a multi-functional electronic load module (3315D, Taiwan) with a DC power supply (SJ 0530D, SEJIN POWER, Korea). All AC impedance measurements were performed with a Solatron 1260 Frequency Response Analyzer (FRA) and a Solatron 1287 Electrochemical Interface (EI). The FRA generates an AC signal in the frequency range of 100 kHz–100 mHz. The EI controls the amplitude of the AC signal placed between the working and reference electrodes with an excitation voltage of 10 mV. The measurements were taken in order to ensure a linear response.

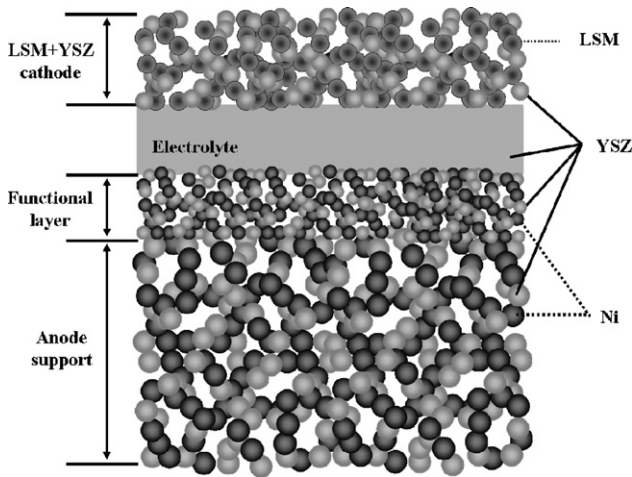


Fig. 2. Schematic of anode-supported SOFC single cell with a tape-casting anode support and an anode functional layer.

### 3. Results and discussion

#### 3.1. Ni–YSZ anode

A schematic of the SOFC single-cell is given in Fig. 2. The porous anode support was manufactured by a tape-casting process and the functional layer (FL) was made by a dip-coating process using NiO–YSZ composite powder [5,6]. Functionally-graded electrode structures are known to be favourable for both electrochemical reaction and mass transport.

The mercury porosimetry data shown in Fig. 3 indicates that the functional layer has a smaller pore-size ( $<0.3 \mu\text{m}$ ) than that of the anode support. The anode support layer has an effective pore structure in view of its high porosity ( $>47\%$ ) and large pore-size ( $>1.1 \mu\text{m}$ ). Theoretical studies show that the TPB length in an electrode is inversely proportional to the grain size and can be optimized by the pore-size and porosity [8]. Note

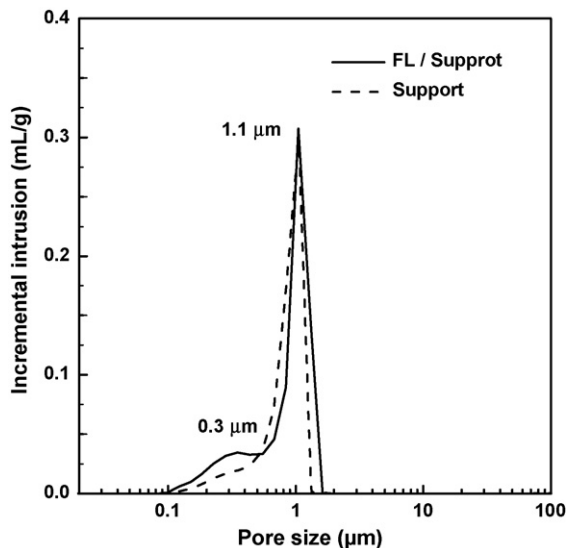


Fig. 3. Pore-size distributions of SOFC anodes measured by mercury porosimetry.

that the grain size of the dual composite powder ( $<0.42 \mu\text{m}$ ) is much smaller than that of commercial anode materials (few microns). It can be inferred that there are a considerable member of Ni–YSZ-pore TPBs at the contiguous region in the electrolyte. Therefore, the efficiency of the anodic reaction can be increased considerably, as the electrochemical reaction mainly occurs there.

Scanning electron micrographs of the microstructure of a YSZ skeleton made from etching the nickel phase in the anode FL (Fig. 4(a)) and the anode support (Fig. 4(b)) of the Ni–YSZ anode with hydrochloric acid are shown in Fig. 4. The microstructures are quite different in terms of uniformity, connectivity, porosity, and grain size. The functional layer made from the composite powder is composed of a well-connected and highly entangled YSZ network by comparison with the anode support. Hydrogen can be oxidized by electrochemical reactions combined with oxygen ions transferred from the interior of solid electrolyte grains to the TPBs with simultaneous discharge and delivery of electrons to the metal network. Impor-

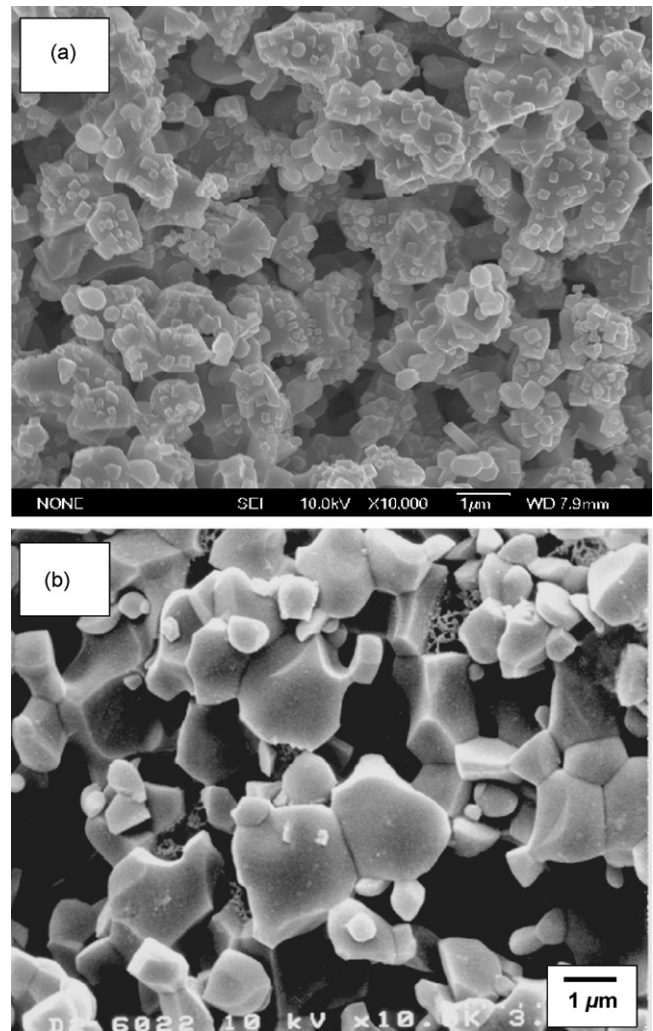


Fig. 4. Scanning electron micrographs of YSZ skeleton made from etching the metal phase in a Ni–YSZ electrode with hydrochloric acid (HCl): (a) anode functional layer manufactured by dip-coating on tape-casting anode support with NiO–YSZ composite powder; (b) anode support manufactured by tape-casting.

tantly, the FL shows high porosity (>40%). Therefore, from the interpenetrated structure among the Ni–YSZ-pores, the produced electrons and water vapour are delivered back to the anode through the conducting phase and pores, respectively. A completely different microstructure from the skeleton of the FL is observed in Fig. 4(b). The YSZ network lacks uniformity due to the fundamental problem of adequate mixing of components during the forming process. The relatively high content of nickel phase of the anode support can account for the irregular distribution of pores and YSZ grains.

### 3.2. YSZ electrolyte

For SOFC technology, the synthesis of a thin and dense electrolyte is important for reducing the ohmic resistance through the electrolyte and improving the performance at reduced temperature. In order to investigate the effect of electrolyte thickness on single-cell performance, the thickness was controlled accurately on the anode support by a dip-coating process. The support was manufactured by a die-pressing process using a NiO–YSZ composite powder. Thin and dense YSZ electrolyte layers were readily synthesized via the sol–gel method as it provides fine structure and high reactivity compared with the conventional ceramic colloidal process (see Fig. 1). The YSZ sol can penetrate the anode by capillary action when the solution comes in contact with a porous surface. Therefore, the YSZ electrolyte layer was synthesized by application of a single slurry coating, and the electrolyte thickness was controlled by a repeated sol–gel coating method.

As can be seen in Fig. 5, the single-cell performances show a clear dependency on the electrolyte thickness. When the YSZ electrolyte thickness is reduced from 10.5 to 6.5  $\mu\text{m}$ , the maximum power density (MPD) of the single cells increases from 0.74 to 1.12  $\text{W cm}^{-2}$  (51.4% increase), at 800 °C. The perfor-

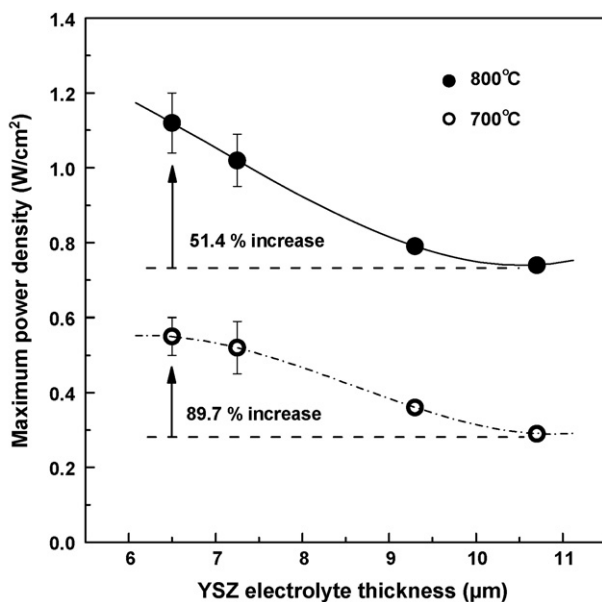


Fig. 5. Maximum power density of single cells with respect to YSZ electrolyte thickness.

mance of single cells in accordance with electrolyte thickness exhibits a wider variation at a lower temperature of 700 °C, namely, the MPD increases from 0.29 to 0.55  $\text{W cm}^{-2}$  (89.7% increase). These results verify that the performance of single cells is governed significantly by the resistance through the electrolyte. From this point of view, the electrolyte thickness should be reduced as much as possible in order to increase the cell performance at reduced temperature.

### 3.3. Single-cell tests

The variation of the area specific resistance (ASR) of anode-supported type single cells with anode structure is shown in Fig. 6. In the case of manufacturing the anode with a composite powder by die-pressing, the ASR (see Fig. 6(a)) of the single cell is quite small, i.e., below 0.31  $\Omega \text{cm}^2$ , at 800 °C. The small ASR is a result of the electrode being fairly homogeneous as well as there being sufficient TPBs and linking of the nickel phase in the electrode. On the other hand, the single cell made from a tape-casting anode shows a large ASR of 1.07  $\Omega \text{cm}^2$ , because the electrode resistance is quite large compared with the anode manufactured using the composite powder. Based on the above results, the composite powder might appear to be an attractive tape-casting material candidate. The NiO–YSZ composite powder is, however, unsuitable for using as a tape-casting material because there is an upper limit of the specific surface-area (5–15  $\text{m}^2 \text{g}^{-1}$ ) of powders with respect to their use as tape-casting materials [9]. High surface-area (HAS) powders (15–20  $\text{m}^2 \text{g}^{-1}$ ) do not readily form slurries for tape-casting as the organic additives, which are characterized by high molecular weight and are used for dispersing and binding the HAS

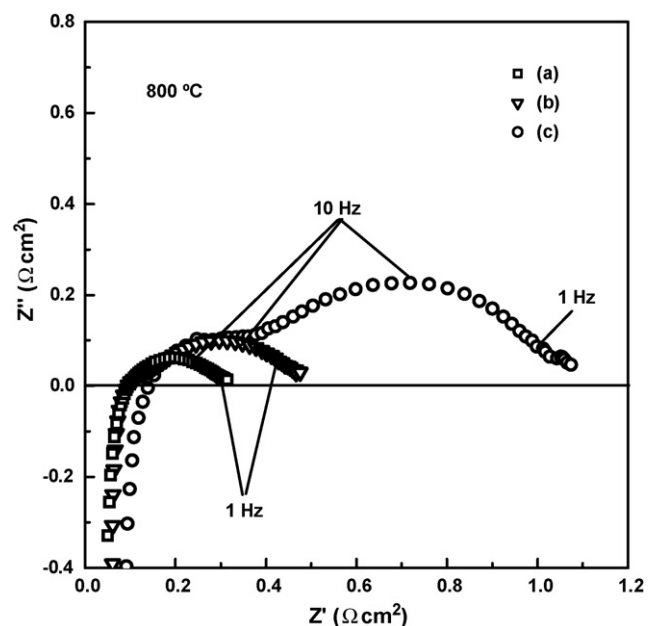


Fig. 6. Area specific resistance (ASR) of anode-supported single cells with variation of anode structure: (a) anode manufactured by die-pressing using NiO–YSZ composite powder; (b) two-layer anode composed of tape-casting anode and functional layer manufactured by dip-coating using NiO–YSZ composite powder; (c) anode manufactured by tape-casting.

powders, cause the slurry to gel easily. The specific surface-area of the composite powder is quite large ( $>23.55 \text{ m}^2 \text{ g}^{-1}$ ), and as such the slurry is unstable in terms of dispersion stability.

One way to utilize the advantages of both the tape-casting process and the composite powder is to use the latter as a functional layer on a tape-casted anode support. Results have shown that a functional layer remarkably reduces the net resistance through single cells using such anodes. As can be seen in Fig. 6(b and c), the total ASR of the anode-supported single cell is reduced from 1.07 to  $0.48 \Omega \text{ cm}^2$ , because the electrode resistance is reduced from  $0.94$  to  $0.39 \Omega \text{ cm}^2$  by using the functional layer. Thus, a functional layer composed of a composite powder markedly reduces the polarization resistance of the interfaces between the anode and the electrolyte.

The  $I$ - $V$  characteristics of single cells shown in Fig. 7 correspond fairly well with the ASR results presented in Fig. 7(a). In all cells, the open-circuit voltages (OCVs) have a stable value between 1.07 and 1.09 V. The findings show that the cell performances are influenced significantly by the anode structure. At the same voltage of 0.7 V, the current density of single cells having a functional layer (Fig. 7(b)) and tape-casting anode (Fig. 7(c)) is  $0.79$  and  $0.45 \text{ A cm}^{-2}$ , respectively. The performances at 0.7 V are  $0.553$  and  $0.315 \text{ W cm}^{-2}$  when converted to power densities, respectively. The single cell made from the composite powder anode gives the highest cell performance among the various cells.

A post-testing scanning electron micrograph of the fractured surface of a single cell made from a tape-casting anode support and a functional layer is given in Fig. 8. Note that the

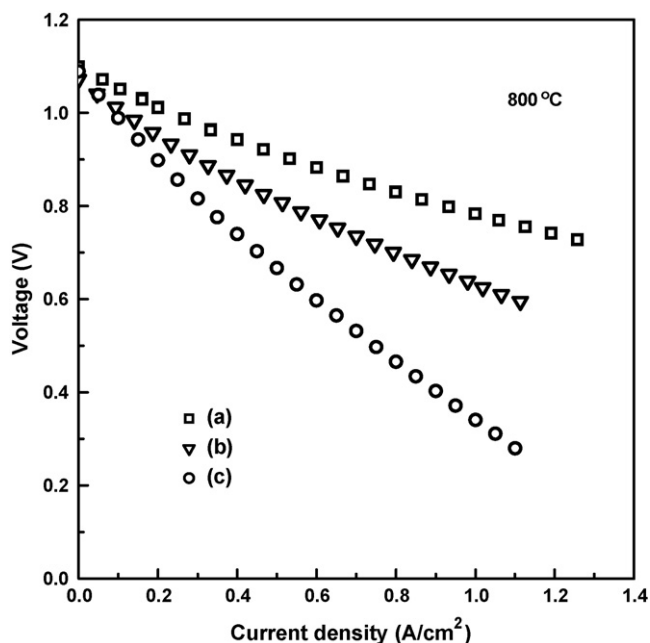


Fig. 7. Current–voltage characteristics of anode-supported single cells with variation of anode structure: (a) anode manufactured by die-pressing using NiO–YSZ composite powder; (b) two-layer anode composed of tape-casting anode and functional layer manufactured by dip-coating using NiO–YSZ composite powder; (c) anode manufactured by tape-casting.

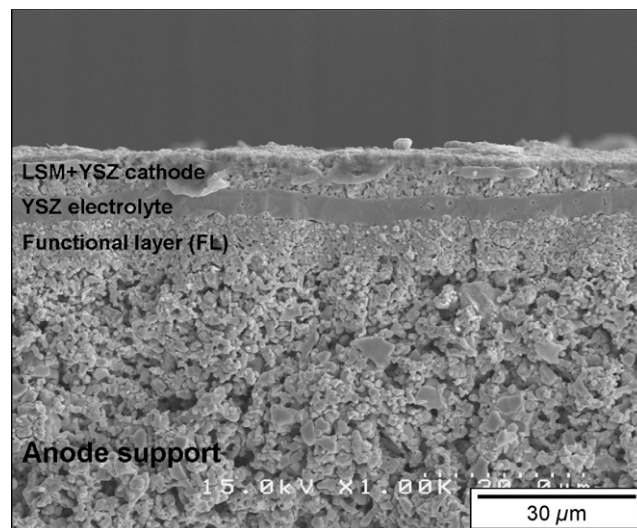


Fig. 8. Scanning electron micrograph of fractured surface of a single-cell with a tape-casting anode support and a functional layer.

electrolyte layer is extremely dense and the thickness is controlled at about  $5$ – $6 \mu\text{m}$ . Porous regions in the anode functional layer and the anode support structure are clearly visible. From the information shown in Figs. 6 and 7, it is clear that the anode functional layer reduces the polarization resistance of the anode|electrolyte interface and enhances the single-cell performance.

Although significant progress has been made, there is still considerable room for improving cell performance via optimizing the cell components. One factor is the mixing homogeneity of the tape-casting anode. As can be seen in Fig. 4(b), the microstructure of the tape-casting anode is very irregular in terms of the distribution and connectivity of pores and YSZ grains. This might reduce the mechanical strength and electrical conductivity of the anode support, which thereby lowers the reliability and performance of the SOFC. Another important factor lies in the thickness of the functional layer. The main purpose of the anode functional layer is to provide reaction sites for electrochemical oxidation of the fuel. Simultaneously, the layer must have sufficient porosity to allow gas transport to the reaction sites. On the other hand, the layer is a source of resistance from a fluid dynamical point of view (see Fig. 3). Therefore, the thickness of the layer must be optimized with respect to the active reaction area and gas flow.

#### 4. Summary

In this work, various types of anode-supported single cells have been manufactured in an effort to improve cell performance. The single-cell performances are highly dependent on the electrolyte thickness and the anode microstructure. When the YSZ electrolyte thickness is reduced from  $10.5$  to  $6.5 \mu\text{m}$ , the maximum power density increases from  $0.74$  to  $1.12 \text{ W cm}^{-2}$  ( $51.4\%$  increase), at  $800 \text{ }^\circ\text{C}$ . The anode functional layer reduces the polarization resistance of the anode|electrolyte interface and enhances the single-cell performance. This is because an effective anode microstructure is formed on the tape-casting anode

support by using a NiO–YSZ composite powder, and this leads to high reactivity and uniformity in the electrodes. Although significant progress has been made, there is still considerable scope for improving cell performance via optimizing the cell components in terms of the thickness and the homogeneity of the anode microstructures.

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