



Microstructure and Electrochemical Behavior of a Structured Electrolyte/LSM-Cathode Interface Modified by Flame Spraying for Solid Oxide Fuel Cell Application

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Plasma-sprayed yttria-stabilized zirconia (YSZ) can be potentially employed as electrolyte layers in solid oxide fuel cells (SOFCs). The formation of a structured electrolyte surface characterized by convex micro deposits generated by only partially molten particles at spraying will increase the specific surface area and subsequently improve the output performance of SOFCs. However, using completely molten YSZ particles during plasma spraying leads to the formation of locally flat surface. In this study, flame spraying was employed to deposit YSZ particles on YSZ substrate using surface-melted particles. The deposition was carried out at different spray distances on YSZ substrate preheated to 650 °C. The surface and cross-section morphology of YSZ particles were characterized by SEM. The electrochemical behavior of single cell with the structured cathode was characterized by the electrochemical impedance spectroscopy. The results show that spray distance exhibits significant influence on the morphology of deposited YSZ particles. The cathode polarization of a structured cathode was decreased by about 30-43% compared to a flat cathode at different temperatures.

Keywords flame spraying, SOFC, structured electrolyte surface, TPB, YSZ

1. Introduction

Plasma-sprayed yttria-stabilized zirconia (YSZ) can be potentially employed as the electrolyte in solid oxide fuel cells (SOFCs) (Ref 1-3). Increasing the output power density of SOFCs through reducing the polarization during its operation is a great challenge facing the practical application of SOFCs. Cathode polarization becomes the dominant factor causing the power losses in SOFCs with

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the decrease in the electrolyte polarization and the optimization of the anode structure (Ref 4, 5). Generally, the electrochemical reaction in a porous $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) cathode is restricted to the triple phase boundaries (TPB) between cathode and the electrolyte surfaces that oxygen can reach to (Ref 6). Several studies reported that a decrease in the cathode polarization is achievable through increasing the TPB and/or the effective electrolyte surface area. Therefore, the formation of a structured convex electrolyte surface will increase the specific surface area and subsequently improve the output performance of SOFCs (Ref 7).

Thermal spraying process has been widely used for developing a cost-effective process to fabricate SOFC components (Ref 8-12). Recent studies showed that atmospheric plasma-sprayed (APS) YSZ can be applied as the electrolyte in SOFCs through a post-spray densification treatment (Ref 13, 14). Most investigations on plasma-sprayed electrolyte were involved in the microstructure optimization through improving heat transfer to spray powders to aim at melting them completely. However, using completely molten YSZ particles during plasma spraying leads to the formation of locally flat surfaces owing to well spreading of liquid droplets on impact. A previous study indicated that the surface roughness of APS YSZ will significantly influence the cathode polarization (Ref 15). A reasonably structured YSZ surface should lead to a high surface area and possibly reduces the cathode polarization. Therefore, in this study, an attempt

was made to create a structured YSZ surface of high surface area through depositing YSZ particles on APS YSZ surface using partially molten particles (i.e., with only particle surface layers melted). To control particle melting, flame spraying was employed to deposit YSZ particles on YSZ substrate using the surface melted particles due to low particle temperature and velocity. The effects of spray distance on the particle deposition behavior and cathode polarization were examined.

2. Experimental

2.1 Materials

A commercially available 4.5 mol% YSZ (4.5YSZ, Shenyang, China) powder was used for examining particle deposition behavior. The powder was manufactured through a sinter-crushing route and exhibited an angular shape as shown in Fig. 1(a) and a nominal particle size

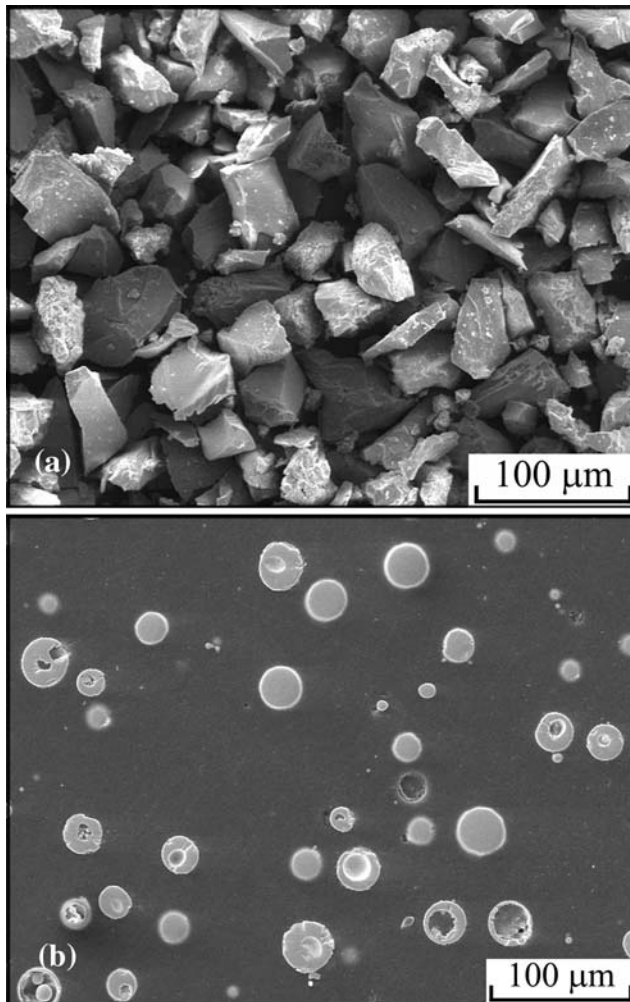


Fig. 1 Morphology of spray powder at different states: (a) starting powder and (b) after spheroidization through APS treatment

range from 23 to 61 μm . The spray powders were then spheroidized by APS before spraying. Spheroidized particles (Fig. 1b) exhibited a particle size range from 16 to 39 μm . The particle size distribution was measured by a laser diffraction particle analyzer (LS 230, Beckman Coulter, Fullerton, CA, USA).

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ was prepared by a conventional solid phase sintering process using a stoichiometric mixture of La_2O_3 , SrCO_3 , and MnCO_3 at 1200 $^\circ\text{C}$ for 24 h in an ambient atmosphere. The sintered powders were crushed and sifted to a size range from 5 to 25 μm (Ref 11).

Commercial 8YSZ pellets of 20 mm in diameter and 0.4 mm thick (Zhuhai, China) were used as substrate for particle deposition and electrolyte for assembling SOFC cell.

2.2 Deposition of Surface-Melted YSZ Particles

Surface-melted YSZ particles were deposited by flame spraying on a polished YSZ substrate at stand-off distances of 60 and 80 mm. A robot was used to manipulate the flame torch back and forth across the substrate surface. During spraying, torch traverse speed was fixed to 800 mm/s. The pressures of C_2H_2 and O_2 were fixed to 0.1 and 0.5 MPa, respectively. The flow rates of C_2H_2 and O_2 were 900 and 800 L/h, respectively. YSZ substrate was preheated to 650 $^\circ\text{C}$ by a flame torch from the back of the substrate. The temperature was monitored using a pyrometer (RAYRPM30L3U, Raytek, Santa Cruz, CA, USA). The microstructure of samples was characterized by scanning electron microscopy (SEM, VEGA II-XMU, TSCAN, Brno, Czech Republic).

2.3 Fabrication of Single SOFC Cells for Electrochemical Measurement

LSM/YSZ/Pt cells were fabricated to test the electrochemical characteristics of the porous LSM/YSZ interface. Figure 2 shows a schematic diagram of electrochemical test cell of LSM/YSZ/Pt. Two kinds of electrolytes were used to deposit LSM cathode. One was commercial 8YSZ pellet ($\varnothing 20 \times 0.4$ mm) prepared by tape casting method, and the other one was the aforementioned 8YSZ with the surface deposited by 8YSZ particles of size distribution ranging from 5 to 25 μm (DTS-Z74, Fujimi, Aichi, Japan) by flame spraying. A LSM cathode layer with a thickness of 20 μm was deposited on two types of electrolyte surface by APS at a standoff distance of 100 mm. Plasma torch was operated at a plasma arc power of 30 kW. A Pt counter-electrode, having the same shape and position as the cathode, was painted on the opposite side of the electrolyte pellet. Reference and counter electrodes were fixed to the pellet through a sintering treatment at 850 $^\circ\text{C}$ for 0.5 h thanks to the use of a Pt paste. The geometrical area of the porous LSM electrode was 0.5 cm^2 . The impedance measurements were carried out in air from 800 to 1000 $^\circ\text{C}$ at an interval of 50 $^\circ\text{C}$. A frequency response analyzer Solartron 1260 and an electrochemical interface Solartron 1287 (Solartron Analytical, Hampshire, UK) were used for the electrochemical impedance measurements. The tests were

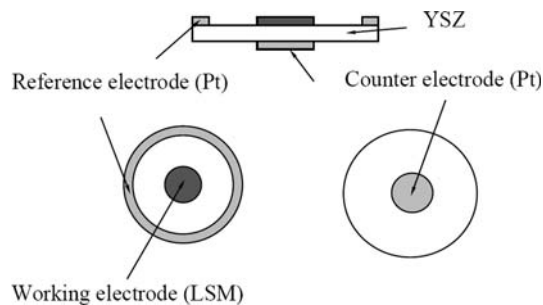


Fig. 2 Schematic diagram of electrochemical test cell of LSM/YSZ/Pt

performed in a frequency range from 0.1 to 10^5 Hz with an amplitude of the AC signal of 100 mV at equilibrium potential in a three electrodes configuration, as shown in Fig. 2.

3. Results and Discussion

3.1 Influence of the Spray Distance on the Morphology of Deposited Particles

Figure 3(a) and (b) shows typical surface and cross-sectional morphology, respectively, of YSZ particles deposited by flame spraying at spray distance of 60 mm. The deposited particles exhibit near spherical shapes. This fact indicates that only the surface layer of particles was melted before impact on the substrate. From the cross section of the particle shown in Fig. 3(b), a gap was observed between spherical particle and substrate, which possibly indicates that the bonding of deposited particle with substrate was not perfect at the periphery of the deposited particle.

When the spray distance was increased to 80 mm, well flattened particles were observed, as shown in Fig. 4(a) and (b). This is due to the fact that the melting degree of particles was improved due to the longer dwelling time of droplets in flame (compared with a stand-off distance of 60 mm). Moreover, it is evident that those particles adhered well with the underlying YSZ substrate. These results suggest that it is possible to deposit YSZ particles with convex morphology using spraying particles with a limited melting. The formation of a structured convex coating surface with semi-melted 8YSZ particles will increase the specific surface area. The estimation showed that the surface area will approximately increase twice when a monolayer of semi-molten YSZ particles will be uniformly deposited on the electrolyte surface.

3.2 Microstructure of Cathode/Electrolyte Interface with the Structured YSZ Particles

Figure 5(a) and (b) shows the cross-sectional microstructure of the cathodes which were deposited on a smooth and a structured electrolyte surface, respectively. It can be clearly observed that the LSM was uniformly

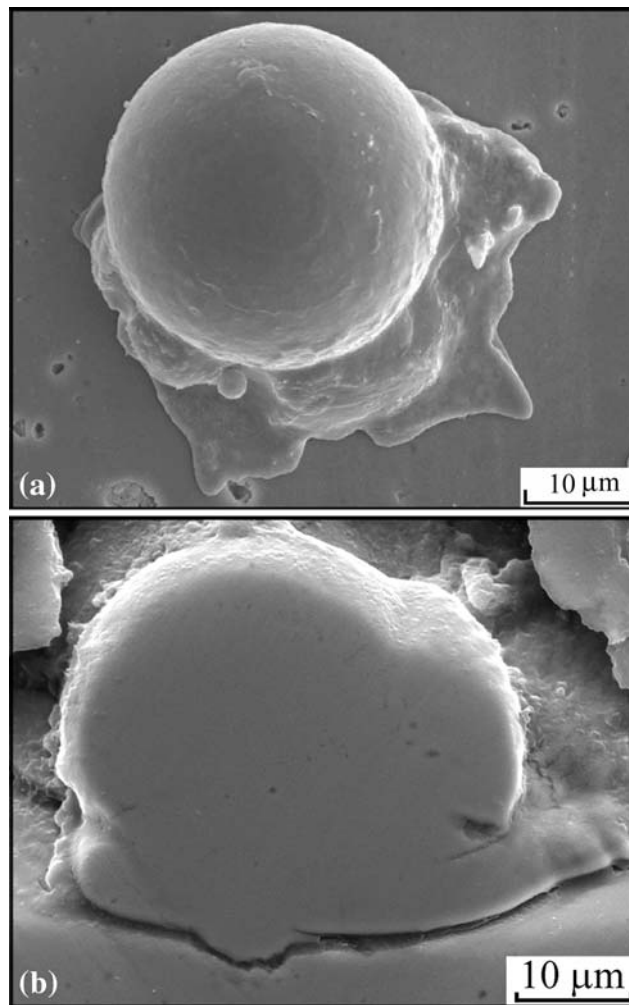


Fig. 3 Morphology of YSZ particles deposited by flame spraying at a stand-off distance of 60 mm: (a) surface and (b) cross section

deposited on the electrolyte surface. The distinct layered structure suggested that the LSM cathode was formed by fully molten particles. The LSM deposits were well adhered to the YSZ electrolyte. As shown in Fig. 5(a), a two-dimensional cathode/electrolyte interface was formed when LSM was deposited on a smooth electrolyte surface. On the other hand, when LSM were deposited onto the structured convex electrolyte surface created by depositing semi-melted YSZ on YSZ electrolyte surface, a three-dimensional cathode/electrolyte interface was constructed, as shown in Fig. 5(b). The previous studies showed that only a fraction of particle interface in a plasma-sprayed ceramic coating is bonded together (Ref 16, 17). The limited interface bonding influences coating performances. With SOFC assembled with plasma-sprayed electrolyte, the non-bonded interface areas will cut off the direct ion transport pathways. The ionic conductivity would be decreased due to the reduction of the effective conduction area. Moreover, the limited bonding across the interface gives rise to bending of the conduction pathways of

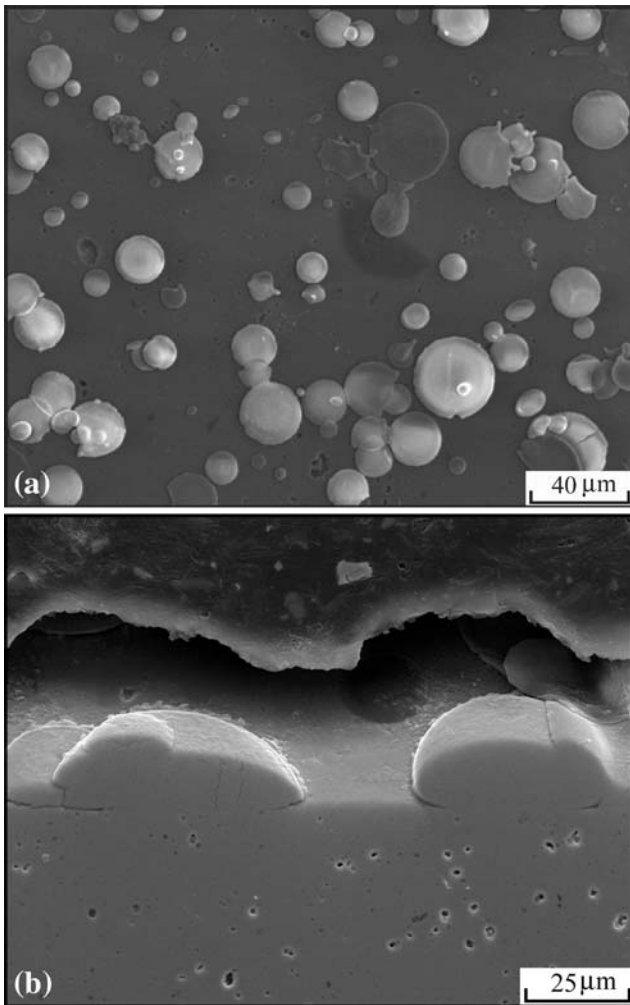


Fig. 4 Morphology of YSZ particles deposited by flame spraying at a stand-off distance of 80 mm: (a) surface and (b) cross section

ions and induces an additional contact resistance (Ref 18). The previous systematical investigations suggested that the temperature of molten spray particle is positively related to an enhanced bonding (Ref 19).

Therefore, using semi-melted droplets may reduce the interface bonding between deposited particles and substrate which is evidenced from microstructure shown in Fig. 5(b). As a result, it is important to improve the bonding between semi-melted YSZ particles and YSZ electrolyte for increasing output performance of SOFC.

Xing et al. (Ref 20) recently reported that when YSZ particles were deposited on a YSZ surface preheated to a temperature higher than 800 °C, most of interfaces between adjacent lamellae were bonded together. This microstructure feature allows oxygen ions to transfer directly across the interface and significantly reduce the contact resistance. Therefore, the bonding between semi-melted YSZ particles and YSZ electrolyte can be improved through controlling YSZ substrate temperature.

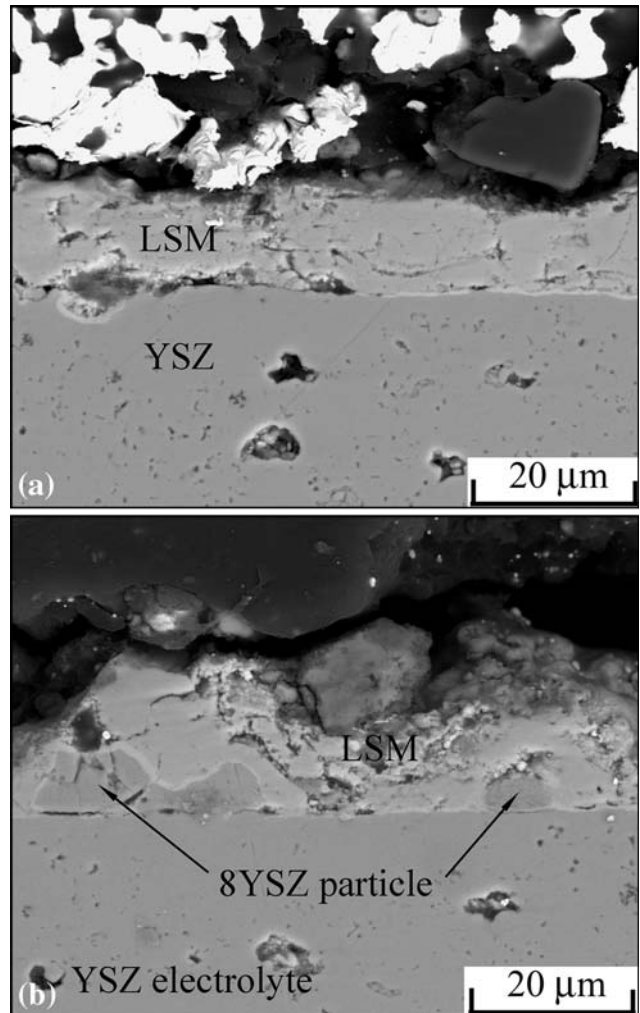
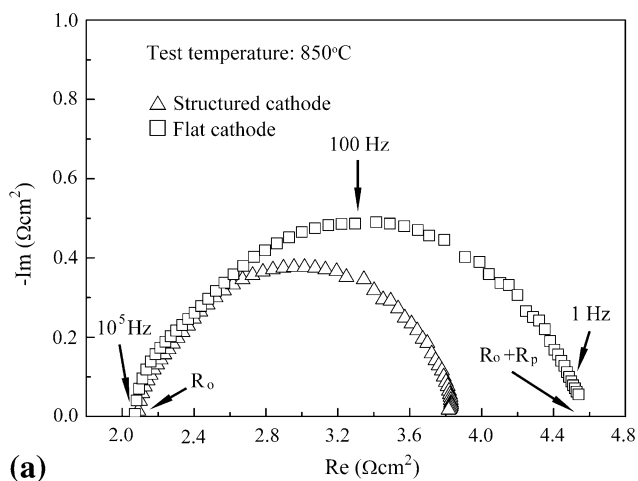


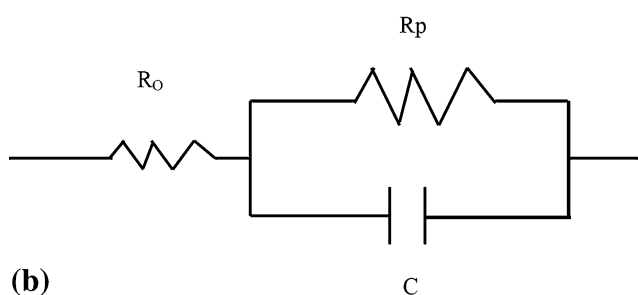
Fig. 5 Cross-sectional morphology of cells: (a) flat cathode and (b) structured cathode

3.3 Influence of Electrolyte/LSM-Cathode Interface Structure on Electrochemical Behavior

Figure 6(a) shows the Nyquist plots measured for a flat cathode and structured cathode at 850 °C. An equivalent circuit, $R_o(R_p(C))$, is illustrated in Fig. 6(b). R_o , R_p and C represent ohmic resistance, polarization resistance and capacitance, respectively. Those data exhibited single arcs, showing that oxygen reduction is controlled by adsorption and desorption (Ref 21, 22). Each curve intercepted the real axis at low and high frequencies. The high frequency intercept R_o is the sum of the total YSZ ionic resistance, LSM electronic resistance and external cell connection resistance contribution. The intercept difference between the low and high frequency of semicircle shows the cathode polarization R_p , which is related to the overall oxygen reduction process. The R_p of the cell with a structured electrolyte is around 1.75 $\Omega\cdot\text{cm}^2$ at 850 °C. The result is approximately one-half of the data reported by Herle et al. (Ref 23), which is about 3 $\Omega\cdot\text{cm}^2$ at 850 °C.



(a)



(b)

Fig. 6 (a) Nyquist diagrams of LSM cathode and (b) equivalent circuit

Table 1 Cathode activation polarization for the flat and structured cathodes vs. measuring temperature

Temperature, °C	Cathode activation polarization, $\Omega\text{-cm}^2$	
	Flat cathode	Structured cathode
800	5.3	3.32
850	2.53	1.75
900	1.62	0.99
950	1.11	0.63
1000	0.77	0.47

Table 1 shows the change in the cathode activation polarization for the flat and structured cathodes versus measuring temperature. Those results showed that the cathode activation polarization depended on the effective electrolyte surface area where the cathode reaction can take place. Moreover, it can be seen that the cathode activation polarization of the cell with a structured cathode is decreased by about 30-43% than that of the cell with a flat cathode at different temperatures. A further increase in the SOFC performance by an optimization of the microstructure of the electrolyte surface should be possible (Ref 24).

The cathode activation polarization is related to TPB of electrode/electrolyte/air. The LSM used in this study is essentially electronically conducting material. LSM was directly deposited on YSZ electrolyte. The transport of ions is restricted to YSZ electrolyte and the transport of

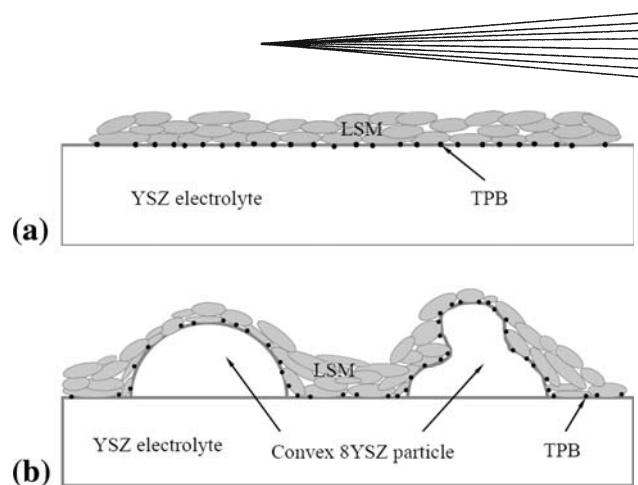


Fig. 7 Cathode/electrolyte interface structures: (a) smooth electrolyte surface with restricted number of active reaction sites and (b) structured electrolyte surface with an increased reaction zone

electrons is restricted to the LSM electrode. This TPB can be characterized by a line, extending along the electrolyte surface, and has the dimensions of cm/cm^2 or cm^{-1} . The electrode kinetics depends upon the TPB length (Ref 25).

The present results indicated that the effective electrolyte surface area is enlarged by depositing semi-melted 8YSZ particles on a smooth YSZ substrate through flame spraying. Figure 7(a) and (b) shows the schematic diagram of two-dimensional interfaces when considering smooth electrolyte surface and three-dimensional interface when considering structured electrolyte surface, respectively. It is clear that the contact area of LSM cathode with YSZ electrolyte can be increased by increasing the total surface area of YSZ electrolyte, thus increasing the TPB length.

Herbstritt et al. (Ref 7) reported that cathode polarization strongly depended on the morphology of the electrolyte surface. Mizusaki et al. (Ref 26) studied the TPB length of the LSM cathode from the SEM images of the cross section of the interface, and showed that the reaction rate was essentially proportional to the TPB length per unit area (L_{TPB}). The present result showed that the cathode polarization was decreased by about 30-43% with the structured cathode compared to the flat cathode at different temperatures. This is mainly attributed to the longer TPB length in the structured cathode than those in the flat cathode per unit apparent area of cell.

4. Conclusions

The present results showed that surface of YSZ electrolyte can be modified by depositing semi-melted YSZ particles on electrolyte surface by flame spraying. The deposition of semi-melted particles led to the increase of the effective electrolyte surface area and the TPB length per unit apparent area of cell. The cathode activation polarization of the cell with a structured electrolyte was decreased by about 30-43% than that of the cell with a flat electrolyte at different temperatures. A further increase in the SOFC performance would be possible by an optimization of the structure of the electrolyte surface.

Acknowledgments

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