



Enhanced Performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) Cathodes with Graded Microstructure Fabricated by Tape Casting

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ABSTRACT :

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) powders with different particle sizes, synthesized through a citrate complexation method and a gel-casting technique, are used to fabricate porous LSCF cathodes with graded microstructures via tape casting. To create porous electrodes with desired porosity and pore structures, graphite and starch are used as pore former for different layers of the graded cathode. Examination of the microstructures of the as-prepared LSCF cathode using an SEM revealed that both grain size and porosity changed gradually from the catalytically active layer (near the electrode-electrolyte interface) to the current collection layer (near the electrode-interconnect interface). Impedance analysis showed that a 3-layer LSCF cathode with graded microstructures exhibited much-improved performance compared to that of a single-layer LSCF cathode, corresponding to interfacial resistance of 0.053, 0.11, and 0.27 $\Omega\text{-cm}^2$ at 800, 750, and 700°C respectively.

Keywords : LSCF, Cathode, Graded microstructure, Tape casting, SOFC.

Received September 19, 2010 : Accepted September 24, 2010

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention due to their high energy efficiency, modularity, and excellent fuel flexibility.¹⁾ However, the cost of the current SOFC systems is still prohibitive for many practical applications. To be economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced. One effective approach to cost reduction is to reduce the operating temperature of SOFCs. As the operating temperature of a fuel cell is reduced, however, the electrode polarization resistances increase rapidly, especially the resistances related to oxygen reduction at the cathode.²⁾

To develop efficient cathodes for low-temperature SOFCs, a number of materials have been explored in recent

years: mixed ionic-electronic conductors (MIEC) with high catalytic activity at lower temperature^{3,4)} and composite electrodes consisting of ionically conducting phases (e.g., yttria-stabilized zirconia or gadolinia-doped ceria) and MIECs.^{5,6)} For a given electrode material, however, the performance of the electrode can be drastically altered by changing its microstructure, including pore and grain sizes, size distributions, and porosity.⁷⁾ In particular, it has been demonstrated that an ideal electrode structure is graded, with fine microstructure of high surface area close to the electrode-electrolyte interface (to maximize the length of the triple-phase boundary) and coarse microstructure of high porosity near the outer layer of the electrode (to facilitate gas transport and current collection).^{8,9)}

Perovskite materials in the $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_{3-\delta}$ family have been extensively investigated as cathode for SOFC due to their high ionic and electronic conductivity and good catalytic activity for the oxygen reduction reaction.^{10,11)} However, $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_{3-\delta}$ cathode material can not

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be directly employed on YSZ electrolyte because of the reaction between (La, Sr)(Co, Fe)O_{3-δ} and YSZ during cathode fabrication, forming a resistive phase of strontium and/or lanthanum zirconate at the interface.^{12,13} In many studies, gadolinia-doped ceria (GDC) or samarium-doped ceria (SDC) has been used as interlayer to prevent the undesirable chemical reactions. It was found that the use of a La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode on an YSZ electrolyte yielded area-specific resistances of about 0.55, 0.65, and 0.85 Ω·cm² at 800, 750, and 700°C using a GDC interlayer between the cathode and zirconia based electrolyte.¹⁴ It was reported earlier that the interfacial polarization resistances of an La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode (with GDC interlayer) on an YSZ electrolyte were about 0.98, 1.67, and 4.02 Ω·cm² at 800, 750, and 700°C, respectively.¹⁵ Reduced electrode polarization resistances were obtained using the same material, deposited on YSZ, and at a lower sintering temperature (1000), equal to approximately 0.18 Ω·cm² at 800°C and 0.6 Ω·cm² at 700°C.¹⁶ Unfortunately, low firing temperature may compromise the long-term stability of the cathode. To date, the studies on LSCF microstructure effect reported in the literatures focus mostly on cathodes of uniform microstructures. In this communication, we report our findings on preparation and characterization of porous La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) cathodes with graded microstructures fabricated by tape casting. The grain size and the porosity were gradually changed from the inner layer (the catalytically active layer near the electrolyte) to the outer layer (the current collection layer). Our efforts focused on controlling the microstructures of the graded porous cathodes in order to minimize the cathodic polarization resistance.

2. Experimental

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} powders with varying particle sizes were synthesized using a citrate complexation method¹⁷ and a gel-casting technique.¹⁸ The surface area and particle sizes of the prepared LSCF powders were determined using the Brunauer-Emmett-Teller (BET, Micromeritics ASAP2000) gas adsorption technique whereas the crystal structure and phase purity were confirmed by X-ray diffraction (XRD, X'Pert, Alpha-1).

Three-layer LSCF electrodes with graded microstructures were fabricated by tape casting. The LSCF powders synthesized by the citrate complexation method and the gel-casting method were used for the inner layer and the middle layer, respectively. Commercial

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} powders (plasma spray powder, Inframat Advanced Materials) were chosen for the outer layer. To tailor the pore size and porosity of each layer, 20 vol% graphite (Alfa Aesar) was added to the LSCF slip for the inner layer and 40 vol% corn starch (Sigma-Aldrich) were added to that for the outer layer. For the middle layer, 15 vol% of graphite and 15 vol% of starch were added. To prepare LSCF slurry for tape casting, proper quantities of LSCF powders and pore formers were ball milled for 12 h with dispersant in a mixture of xylene and ethanol (volume ratio of 1 : 1). Then, two plasticizers (polyalkylene glycol and butyl-benzyl phthalate, Richard E. Mistler, Inc.) and a commercial bonder (polyvinyl butyral, Richard E. Mistler, Inc.) were added to enhance the flexibility and strength of the green tapes. The mixture was further milled for another 12 h. The resultant slurry was casted on a doctor-blade tape casting machine (Richard E. Mistler, Inc.). The inner layer was cast first on the carrier film and allowed to dry in air for several minutes; then, the middle layer and the outer layer were cast similarly one after another. The thickness of each layer (green) was ~20 μm. After drying overnight at room temperature, the three-layer green tape was cut into disks with a diameter of 5 mm. For comparison, a single layer LSCF cathode of ~60 μm thick was also fabricated using the same method. The LSCF powders purchased from Fuelcell Material Co. (surface area of 5.4 m²/g) were used as the precursor and 30 vol% graphite were used as pore formers. In order to characterize the electrochemical behavior of these cathodes with different microstructures, electrolyte-supported symmetrical cells with a configuration of LSCF|SDC|YSZ|SDC|LSCF were used. Dense YSZ pellets of 13 mm in diameter and 1 mm in thickness were prepared by dry pressing and sintering at 1450°C for 5 h. The LSCF tapes were bonded to both sides of YSZ electrolyte using a Sm_{0.2}Ce_{0.8}O_{1.95} (SDC) buffer layer. The SDC buffer layer was prepared by dropping coating a SDC slurry on YSZ surface. After dried at 80°C for 1 h, the symmetrical cells were fired at 1050°C for 2 h with a heating rate of 2°C min⁻¹. Pt mesh was attached to both sides of a symmetrical cell as current collector for electrical measurements. Impedance spectra were acquired using a Solartron 1255 frequency response analyzer, interfaced with an EG&G PAR potentiostat model 273A, in the frequency range of 100 kHz to 0.1 Hz (signal amplitude was 10 mV). The impedance measurements were performed under open circuit conditions at temperatures ranging from 650 to 800°C. All data were collected in 30 min after the desired temperature

was reached. The impedance data were normalized by the electrode area (0.20 cm^2), and divided by two to obtain the area specific polarization resistances of each LSCF individual electrode (of a symmetric cell). Microstructure and morphology of the electrodes were also examined using a scanning electron microscope (SEM, LEO1530).

3. Results and Discussion

Shown in Fig. 1 are some typical XRD patterns of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ powders derived from a citrate complexation method (Fig. 1a) and a gel-casting process (Fig. 1b), together with that for the commercially available LSCF powder (Fig. 1c). The as prepared LSCF powders exhibit the desired crystalline phase (rhombohedral structure) at relative low calcination temperature. The phases were relatively pure because there was no observable evidence of impurity or secondary phases. Table 1 summarizes the microscopic features (specifically, BET specific surface area and primary particle size) of the LSCF powders after ball-milling for 24 h. The surface area (or the mean particle size) of powders were varied greatly with the synthesis methods. The powders derived from the citrate complexation method

and the gel-casting process have specific surface areas of $14.38 \text{ m}^2\cdot\text{g}^{-1}$ and $8.07 \text{ m}^2\cdot\text{g}^{-1}$, respectively. For the commercial powder, it showed the smallest specific surface area ($1.36 \text{ m}^2\cdot\text{g}^{-1}$) and the largest particle size ($0.74 \mu\text{m}$) among the three.

For the LSCF tape cathode, the effect of the pore former on the microstructure was studied. Shown in Fig. 2 are the top views of single-layer cathodes fabricated using different pore formers after firing at 1050°C for 2 h. The amounts of the pore formers used for both samples were $\sim 30 \text{ vol}\%$ (relative to ceramic powders) and the other organic additives were kept the same. Clearly, the type of pore formers significantly influenced the microstructures. When graphite was used as pore former, the pores are relatively small (the average pore size was about $1\text{--}2 \mu\text{m}$) and uniformly distributed, as seen in Fig. 2a. In contrast, when corn starch was used as pore former (Fig. 2b), the pores are larger and distributed less uniformly, producing a more open porous microstructure. Thus, the combination of different pore formers may create graded porous cathodes for solid oxide fuel cells. For example,

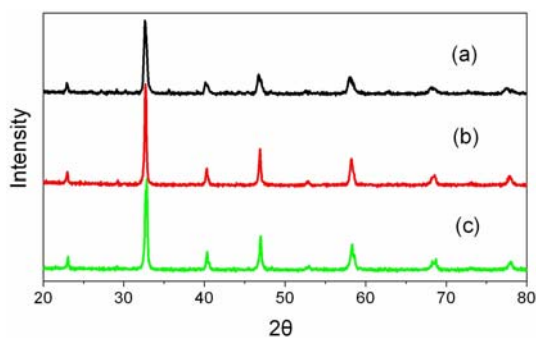


Fig. 1. XRD patterns of LSCF powders derived from (a) a citrate method (calcined at 900°C for 2 hours) and (b) a gel-casting method (calcined at 950°C for 10 hours) in comparison with that for (c) a commercial LSCF powder as received (Inframat Advanced Materials).

Table 1. Surface areas and average particle size of LSCF powder

Powder type	Calcination temp. ($^\circ\text{C}$)	BET specific surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Average particle size (μm)
Citrate Method	900	14.3817	0.070
Gelcasting Technique	950	8.0732	0.124
Commercial Powder	-	1.3606	0.735

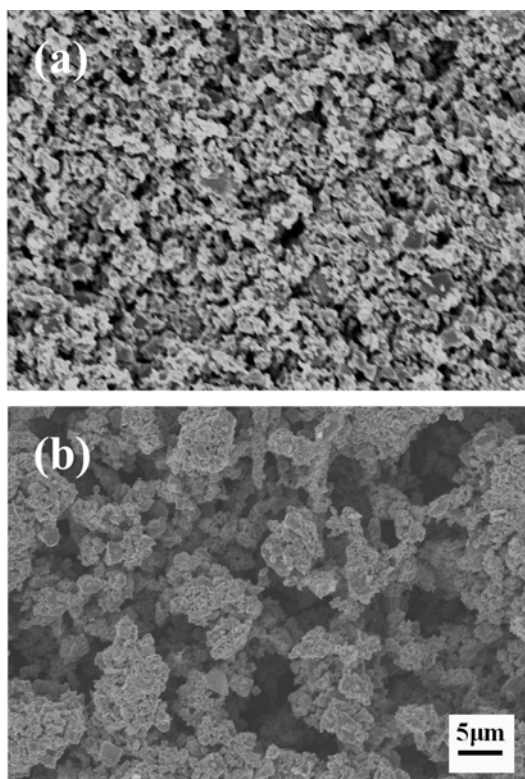


Fig. 2. Top view of tape cast LSCF cathodes prepared using (a) graphite (30 vol%) and (b) corn starch (30 vol%) as pore formers.

fine microstructures with smaller pores and larger surface areas can be created using graphite as pore former for the inner layer of the cathode (adjacent to the electrolyte-electrode interface) to increase the number of active sites for oxygen reduction, whereas coarse microstructures with larger pores can be created using corn starch as pore former for the outer layer of the cathode to facilitate gas transport. In order to match the sintering behavior of the two layers, we introduced a middle layer between the inner layer and the outer layer using a mixture of graphite and corn starch as pore formers.

Shown in Fig. 3a is a cross-sectional view of a 3-layer cathode with graded microstructures supported on a dense

YSZ electrolyte. In general, the 3-layer porous structures show good adhesion to the electrolyte support without observable cracks or other large defects. The LSCF cathodes with thickness about 50 μm are graded in both porosity and grain size. Quantitative analysis of cross-sectional SEM images reveals that the inner layer (Fig. 3b) has finer grains (0.5 μm diameter) and lower porosity ($\sim 30\%$), the middle layer (Fig. 3c) has slightly larger grain size ($\sim 1 \mu\text{m}$) and coarser microstructure, and the outer layer (Fig. 3d) have even larger grains ($\sim 1.5 \mu\text{m}$ diameter) and higher porosity ($\sim 50\%$). The top layer with large interconnected pores allows rapid transport of oxygen molecules and the inner layer offers considerably long

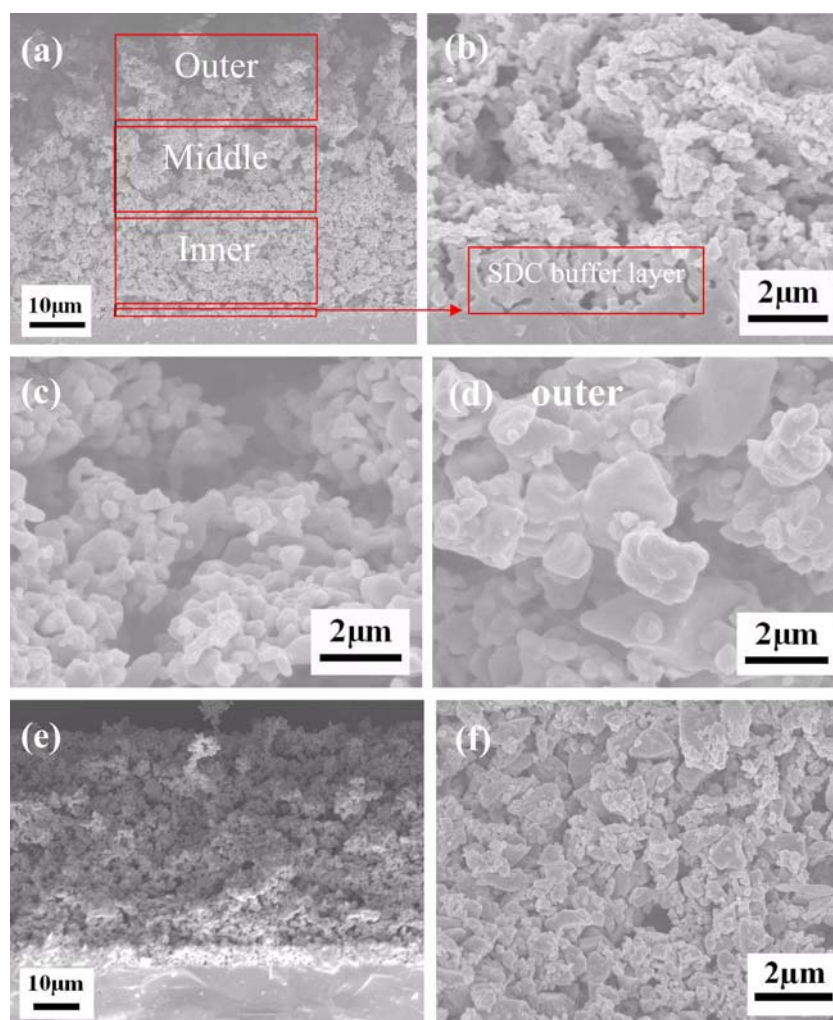


Fig. 3. (a) A typical cross-sectional view of a 3-layer LSCF cathode with graded microstructure and higher magnification of (b) the inner layer, (c) the middle layer, and (d) the outer layer; (e) A typical cross-sectional view of a 1-layer LSCF cathode and (f) higher magnification of the 1-layer cathode.

triple phase boundary for catalytic reactions. To make a comparison, a cross-sectional view of a 1-layer LSCF cathode is shown in Fig. 3e. The thickness is $\sim 50 \mu\text{m}$, similar to that of the 3-layer cathode. The microstructure is relatively uniform through the electrode.

Shown in Fig. 4 are several typical impedance spectra of the 1-layer and 3-layer LSCF cathodes (typical microstructures of the cells were presented in Fig. 3) as measured in a symmetrical cell with a configuration of LSCF|SDC|YSZ|SDC|LSCF in air at different testing temperatures. In order to clearly show the difference in the electrode polarization behavior, the ohmic resistances were removed from the impedance data. The interfacial polarization resistances, R_p , were determined from the sizes of the impedance loops for each electrode under open circuit conditions. As can be seen in Fig. 4a, the 1-layer LSCF cathodes exhibited area specific resistances (ASR) of 0.088, 0.186, 0.43, and $1.16 \Omega\text{-cm}^2$ at 800°C , 750°C , 700°C , and 650°C , respectively, similar to those reported in the literature.¹⁵⁾ In contrast, the cells with 3-layer LSCF electrodes of graded microstructure displayed much better performance (Fig. 4b). The electrode polarization resistances were reduced to about 0.053, 0.11, 0.27, and $0.65 \Omega\text{-cm}^2$ at the corresponding temperatures.

Fig. 5 shows the impedance spectra for cells with a 1-layer LSCF and a 3-layer LSCF electrodes measured at 700°C in different partial pressures of oxygen. The

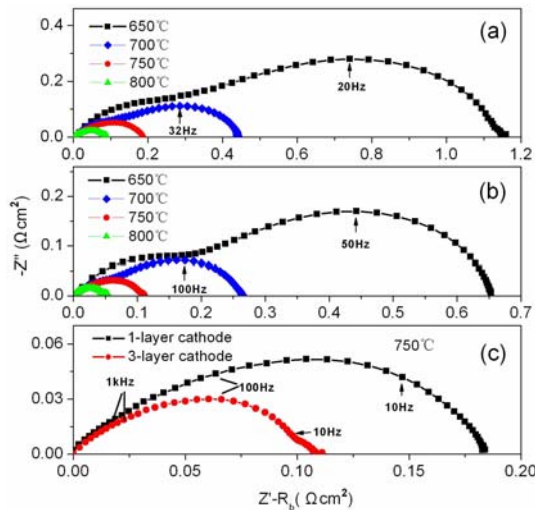


Fig. 4. Typical impedance spectra (Nyquist plots) measured in air under open circuit conditions for symmetrical cells with (a) 1-layer and (b) 3-layer LSCF electrodes. (c) Impedance spectra of a 3-layer cathode, compared to the response from a 1-layer cathode measured in air at 750°C .

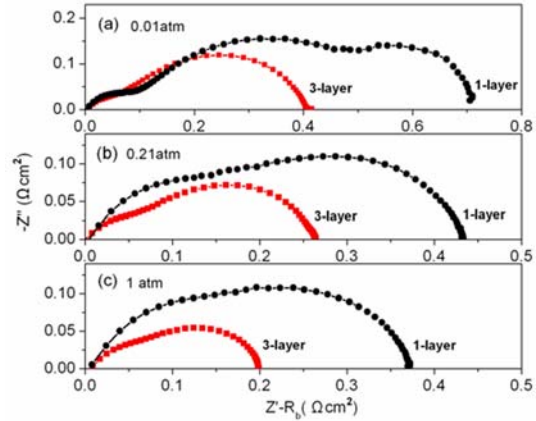


Fig. 5. Typical impedance spectra for 1-layer and 3-layer LSCF cathodes measured under open cell conditions at 700°C in different partial pressures of oxygen: (a) 0.01 atm.; (b) 0.21 atm., and (c) 1 atm.

polarization resistances corresponding to the high-frequency semicircle showed weaker dependence on oxygen partial pressure whereas the low-frequency semicircle showed much stronger dependence on oxygen partial pressure, as similarly reported by others.^{11,19)} When the partial pressure of oxygen was very low (0.01 atm), the electrode performances seem to be dominated by the resistance to mass transport through the porous cathodes, as seen in Fig. 5(a). In contrast, when the partial pressure of oxygen is sufficiently high (in air or oxygen), the spectral features (e.g., the shape) of the 3-layer cathode are similar to those of the 1 layer cathode, as seen in Fig. 4(c), Fig. 5(b), and Fig. 5(c), implying that the 3-layer cathodes with graded microstructures reduced (i) the impedance to charge transfer (i.e., oxygen reduction) by increasing the number of active sites near the electrolyte-cathode interface (since the inner layer has finer microstructure) and (ii) the impedance to mass transfer (oxygen molecules transport) through the outer layer of the cathode by increasing the pore size and porosity. While it is clear that the polarization impedances of the 3-layer cathode are much smaller than those of the 1-layer cathode under similar conditions, it is difficult to deduce the details of the corresponding cathode processes from these impedance data. Indeed, impedance spectroscopy is a very powerful approach to separate the ohmic resistances from the electrode polarization resistances so that we are able to unquestionably determine the performance of an electrode. However, it is extremely difficult, if not impossible, to deduce reaction mechanisms and the nature of electrode processes from

impedance spectra alone. Additional measurements are necessary in order to separate the contributions from different electrode processes relevant to oxygen reduction.

Shown in Fig. 6 are the area specific polarization resistances of LSCF cathodes (3-layer and 1-layer) fabricated by tape-casting in the present work, together with data reported in the literature for LSCF cathode deposited on GDC or YSZ electrolyte. Clearly, the 3-layer LSCF cathodes fabricated by tape-casting display lower interfacial resistance than the 1-layer cathodes fabricated by other methods, including screen printing,^{15,16} spray pyrolysis²⁰ and brush painting.²¹ At 800°C and 700°C, for example, the polarization resistance for the 3-layer graded cathode is about 0.053 and 0.27 $\Omega\cdot\text{cm}^2$, respectively, in contrast to 0.17 and 0.7 $\Omega\cdot\text{cm}^2$ at the same temperatures for screen printed cathode and 1.36 $\Omega\cdot\text{cm}^2$ at 700°C for the deposited film by spray pyrolysis. Compared to the LSCF/CGO/YSZ electrode prepared by screen printing and sintered at 1100°C, the improvement in performance of the 3-layer graded cathode is more dramatic, approaching an order of magnitude at operating temperatures 650-800°C. Interfacial resistances of the 1-layer LSCF cathode prepared by tape casting were also indicated in Fig. 6. For the thicknesses of both were 50 μm , the graded cathode showed a lower interfacial resistance than that

of the 1-layer cathode, e.g., 0.27 $\Omega\cdot\text{cm}^2$ vs 0.43 $\Omega\cdot\text{cm}^2$ at 700°C. Moreover, the performance of the 3-layer graded LSCF cathodes was stable over a period of 50 hours operation although additional testing over a longer period of time is necessary to evaluate the long-term stability.

4. Conclusions

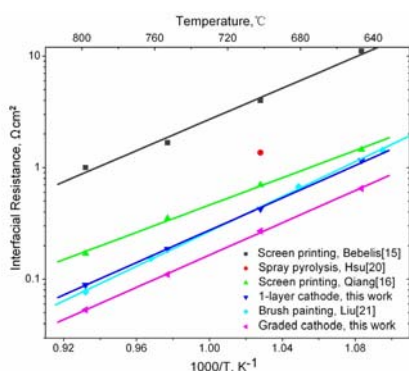
The 3-layer graded porous LSCF cathodes were successfully fabricated by a low-cost tape casting process using graphite and corn starch as pore former. The fabricated cathodes were graded in both grain size and porosity, from finer microstructure for the inner (catalytically active) layer to coarse microstructure for the outer (current collection) layer. Impedance analysis of symmetrical cells using YSZ electrolyte at operating temperature of 650-800°C indicated that the 3-layer cathodes with graded microstructures have much lower interfacial polarization resistances (i.e. 0.053 and 0.27 $\Omega\cdot\text{cm}^2$ at 800 and 700°C, respectively) than the 1-layer cathode fabricated by other methods. The results suggest that the performance of LSCF cathodes can be considerably improved by microstructure optimization and that low-cost SOFCs can be fabricated using a simple tape casting process.

Acknowledgement

This work was supported by the U.S. Department of Energy SECA Core Technology Program under award number DE-NT0006557 and by the WCU Program at UNIST from the Korean Ministry of Education, Science, and Technology. Lifang Nie thanks the fellowship support by the China Scholarship Council.

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Cathode composition	T _{sintering}	Interlayer/electrolyte	Thickness	Note
La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	1100°C for 3h	GDC/YSZ	~20 μm	Ref.[15]
La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	1000°C for 2h	None/YSZ	28±7 μm	Ref.[16]
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	1000°C for 2h	None/GDC	~5 μm	Ref.[20]
La _{0.5} Sr _{0.2} Co _{0.5} Fe _{0.8} O ₃	1000°C for 2h	None/YSZ	~15 μm	Ref.[21]
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	1050°C for 2h	SDC/YSZ	~50 μm	1-layer, this work
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	1050°C for 2h	SDC/YSZ	~50 μm	3-layer, this work

Fig. 6. Comparison of the interfacial polarization resistances of LSCF cathodes on YSZ electrolyte, fabricated using different techniques. The electrode polarization resistances were determined from impedance spectroscopy under open circuit conditions in air.

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