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Technical Communication

Fabrication and characterization of functionally-graded LSCF cathodes by tape casting

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ABSTRACT

Functionally graded cathodes for solid oxide fuel cells are prepared using a tape casting process. The microstructures of the cathodes are gradually changed from a finer LSCF layer with smaller grains (to increase the number of active sites for oxygen reduction) to a coarser LSCF layer with larger grains and higher porosity (for efficient current collection and fast gas transportation). The microstructure and electrochemical properties of the porous electrodes are characterized using scanning electron microscopy and electrochemical impedance spectroscopy, respectively. The cathodic polarization resistance of test cells with functionally-graded LSCF cathodes fired at 1050 °C is reduced to 0.075 Ω cm² at 700 °C and 0.036 Ω cm² at 750 °C, demonstrating peak power densities of 371.5, 744.6, and 1075.3 mW/cm² at 700, 750, and 800 °C, respectively.

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1. Introduction

Solid oxide fuel cells (SOFC) are the cleanest and most efficient systems for direct conversion to electricity of a wide variety of fuels, from hydrogen to hydrocarbons, coal gas, bio-derived fuels, and other renewable wastes [1–6]. The performance of the existing SOFCs is often limited by the oxygen reduction reaction (ORR) at the cathode, more so at lower operating temperatures [7,8]. This is especially true for SOFCs based on thin-film electrolyte membranes, the resistances of which are relatively small [9,10]. Several approaches have been explored to improve cathode performance, including the development of electro-catalytically active cathode materials or the use of

composite cathodes containing catalytically active phases such as Sr_{1-x}Sm_xCoO_{3-δ} (SSC), Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-δ} (BSCF), and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}-Ce_{0.8}Sm_{0.2}O_{2-δ} [11–13]. Another effective approach is to create functionally graded structures to enhance the charge and mass transport processes while minimizing the mismatch in physical properties between the electrode materials and the electrolytes, effectively overcoming the problems associated with dissimilar materials [14–20]. However, the long term stability of the new materials and the additional interfaces between the graded materials is a concern. Another strategy is to tailor the microstructure of the cathode layer by layer: with finer microstructure of high surface area closer to the electrode–electrolyte interface (to

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maximize the length of the triple-phase boundary) and coarser microstructure of higher porosity near the outer-layer of the electrode (to facilitate gas transport and current collection) [15,21–23]. In particular, it has been demonstrated that improved performance was achieved through microstructure optimization involving graded multi-layer cathodes [24].

$\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) based cathodes have attracted much attention for low-temperature SOFCs because they not only have high electronic and oxygen ion conductivity but also show good compatibility with YSZ electrolyte if doped ceria is used as a buffer layer between YSZ and the LSCF cathode [25–29]. Recently, we developed a tape casting process to fabricate LSCF cathode [30], which showed good performance and repeatability for SOFC application. However, the microstructures of the LSCF cathodes need to be further optimized to achieve higher performance.

In this paper, we report our finding on cathodes graded in microstructure for SOFCs fabricated by tape casting. The LSCF cathodes, consisting of fine inner-layer and coarse outer-layer, were fabricated using a tape casting process, a technique widely used for fabrication of thin and thick films of porous and dense ceramic materials. The observed electrochemical performances of the graded cathodes are very encouraging for the development of YSZ fuel cells operated at temperatures below 800 °C.

2. Experimental

2.1. Fabrication of functionally graded LSCF tape

In this study, LSCF were prepared by tape casting using a commercially available LSCF powder (LSCF-C fuel cell materials Inc.), LSCF-CA powder prepared by a citric acid complexing method [31], and graphite powders (Aldrich). Then, two kinds of powders were separately mixed with ethanol and xylene to form an aqueous slurry containing binders (Polyvinyl Butyral, PVB, Richard), plasticizers (Polyalkylene Glycol, PAG and Butyl Benzyl Phthalate, BBP, Richard) and a dispersant (Menhaden Fish Oil, Richard E. Mistler). The relative amounts of PVB, PAG, BBP, and fish oil were ~6%, 5%, 3%, and 3%, respectively, of the total weight of the oxides. Graphite was also added to the slurry in a quantity equal to 5% and 25% of the total weight of the oxides for fine inner-layer and coarse outer-layer, respectively. All tape cast slurries were prepared using a two-stage milling process. The initial slurry contained only powder, solvent and dispersant and was ball-milled for 24 h prior to addition of the other constituents. The mixture was ball-milled for another 24 h to obtain a uniform and stable slurry, which was then degassed at room temperature under vacuum of $\sim 1 \times 10^{-1}$ bar for 5 min before tape casting. Graded LSCF tape with one coarse outer-layer (powder from commercial LSCF) and one fine inner-layer (powder from citric acid method) were co-casted by tape casting (TCS). Further, a single layer LSCF tape (powder from commercial LSCF) was also casted for comparison. The thickness of the graded tape and the single-layer LSCF tape were 40 μm . The LSCF tapes were allowed to dry overnight before punched to pieces of LSCF green tapes.

2.2. Fabrication of symmetrical cells and anode supported cells

2.2.1. Symmetrical cell

The symmetrical cells based on GDC were fabricated as follows. GDC pellets were prepared by pressing commercial GDC powder (SY, ULSA) in a cylindrical stainless steel mold (13 mm in diameter) with a uniaxial dry press at a pressure of 300 Mpa for 1 min, followed by sintered at 1450 °C for 5 h. The density of the pellets was about 98% of the theoretical value as determined by the Archimedes' method. The LSCF tapes were bound on GDC surface using a GDC slurry, followed by firing at 1050 °C–1150 °C for 2 h.

2.2.2. Anode supported cell

Anode supported cells with a configuration of NiO–YSZ (800 μm) | NiO–YSZ active layer (15 μm) | YSZ electrolyte (15 μm) were prepared by co-casting method as described elsewhere [32]. After dried in air for overnight, the green tape was punched to 13 mm in diameter and followed by sintering at 1400 °C for 5 h to get half cells. The LSCF tapes were then bound onto YSZ surface by a GDC slurry, followed by firing at 1050 °C for 2 h. The configuration of symmetrical cells and anode supported cells are shown in Fig. 1.

2.3. Characterization of microstructure and electrochemical performance

The specific surface areas of LSCF powders as well as the LSCF tapes were characterized by BET surface-area measurements (Micromeritics, ASAP 2000). The morphology and microstructure of the cells were examined using a thermally assisted field emission scanning electron microscope (SEM, LEO 1530).

Both symmetrical cells and anode supported cells were used for electrochemical measurement. Pt mesh was attached to both sides of a symmetrical cell as current collector for electrical measurements. The cells were electrochemically characterized with a Solartron 1287 potentiostat coupled with a Solartron 1255 HF frequency response analyzer, in the frequency range of 100 kHz–0.01 Hz (signal amplitude was 10 mV). Each anode supported cell was mounted on an alumina tube and tested with humidified (3% H_2O) hydrogen as fuel and ambient air as oxidant.

3. Results and discussion

The microstructures and the specific surface areas of the prepared LSCF tapes were analyzed using SEM and BET. As summarized in Table 1, the surface areas of the LSCF-C powder and LSCF-CA powder were about 5.4 and 13.62 m^2/g ,

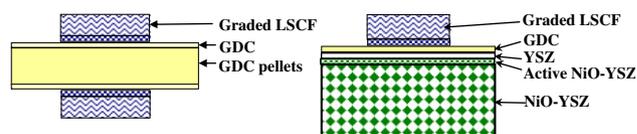


Fig. 1 – Schematic cross-sectional views of (a) a symmetrical cell and (b) an anode-supported cell used for performance evaluation of LSCF electrodes.

Table 1 – BET surface areas of powders and fired tapes used in this study.

Materials/tapes	Surface area (m ² /g)
Commercial powder	5.4
Citrate powder	13.62
Single tape-1050	3.87
Graded tape-1050	6.27
Graded tape-1100	4.40
Graded tape-1150	3.90

respectively. Due to the high surface area of the LSCF-CA powder, it may increase the number of active sites for oxygen reduction when it is used as the fine layer of the cathode, hence enhancing the cathode performance. With the two powders as precursors, the specific surface area of the graded LSCF tape cathode was 6.27 m²/g when fired at 1050 °C for 2 h, which is much higher than that of a single layer LSCF tape cathode prepared using the commercial powder, 3.87 m²/g. The results are consistent with the SEM analysis. Shown in Fig. 2a–e are the cross sectional views of two different LSCF tapes fired at 1050 °C for 2 h. Fig. 2a shows an image of a single LSCF tape cathode fabricated from a commercial powder. A homogeneous distribution of particles and pores is seen throughout the cathode, from the cathode/electrolyte interface to the top of the cathode. No distinguishable variation in microstructures is observed across individual layers. Fig. 2b shows a clear view of the graded microstructure with 10 μm fine inner-layer and 30 μm coarse outer-layer. Fig. 2c and e shows the coarse outer-layer with 1–3 μm grain size and fine inner-layer with 50–300 nm grain size, respectively. The interface of the two graded layers changed gradually, and the buffer layer GDC enhanced the interface of GDC and LSCF, as shown in Fig. 2d and e.

Fig. 3 illustrates the effect of microstructure on the interfacial resistance. It is observed that, at a given temperature, the interfacial polarization resistances of graded tape

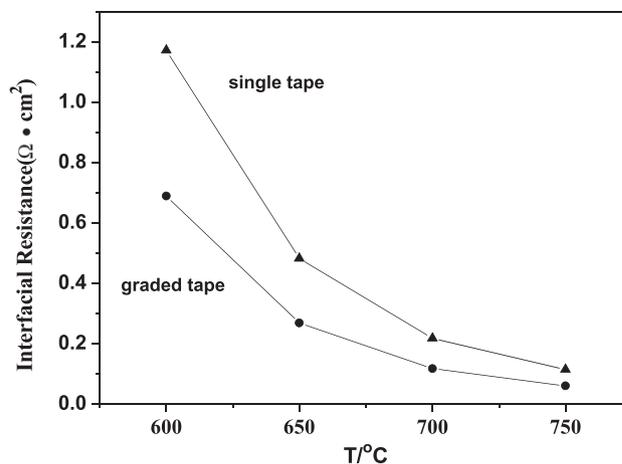


Fig. 3 – Interfacial polarization resistances of different LSCF tape electrodes as measured in symmetrical cells in ambient air.

cathodes (0.036 Ω cm² at 750 °C) are about one-half of that for a single tape (0.061 Ω cm² at 750 °C). The graded tape cathodes dramatically increased the cathode performance of LSCF, since fine inner layer showed higher surface area and smaller grain size, which significantly increases the number of active sites for oxygen reduction compared to a single coarse layer LSCF cathode.

However, further increasing the firing temperature reduced the specific surface area of the graded tape cathode significantly, because the higher firing temperature caused grain growth and porosity decrease. As shown in Table 1, the specific surface area decreased from 6.27 to 3.90 m²/g as the firing temperature was increased from 1050 to 1150 °C. The significant decrease in specific surface area of the cathode resulted in dramatic loss in the number of active sites and increase of the polarization resistances. Fig. 4 shows the effect

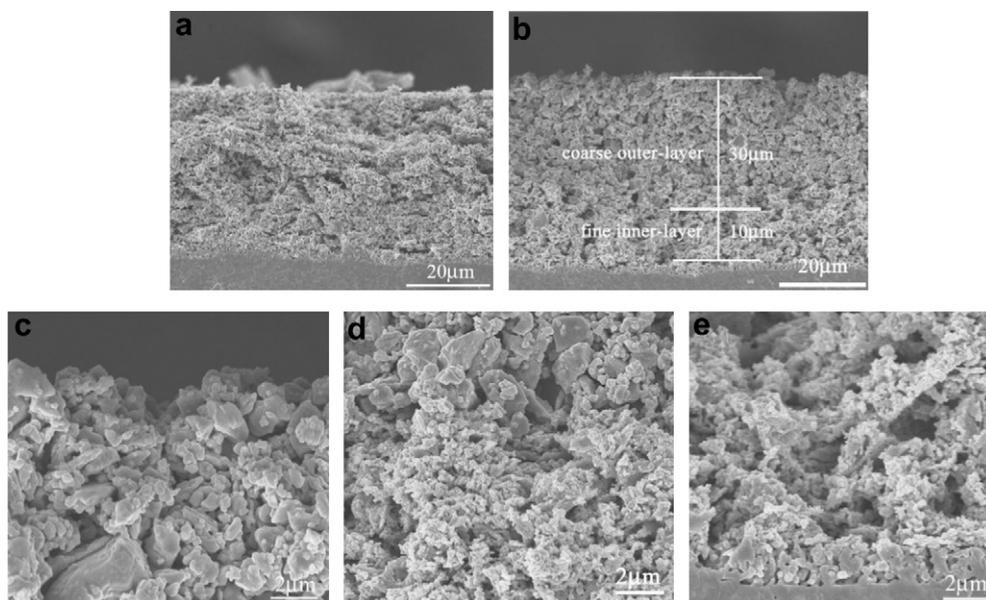


Fig. 2 – Cross sectional views (SEM images) of a single-layer LSCF cathode and a graded LSCF tape electrode fired at 1050 °C: (a) a single tape; (b) a graded tape; (c) the coarse outer-layer; (d) the interface of the graded LSCF tape; (e) the fine inner-layer.

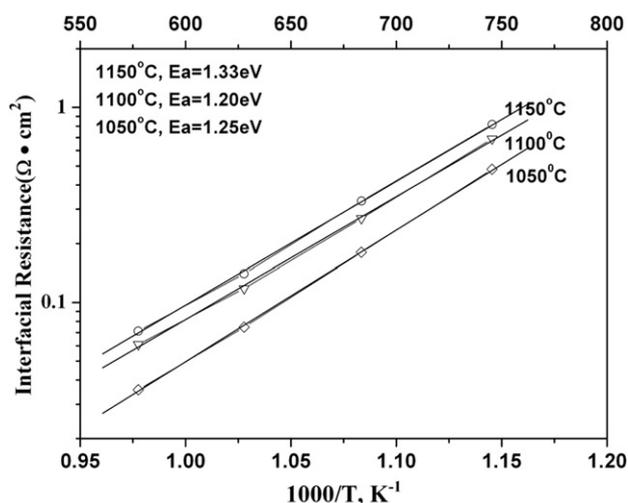


Fig. 4 – Electrode polarization resistance, as measured in symmetric cells, of graded LSCF tape electrodes fired at different temperatures.

of firing temperature on the interfacial resistance of graded tape in the symmetric cell study. The LSCF tape fired at 1050 °C (g-tape-1050) displayed better performance than the tape fired at higher temperatures.

Fig. 5 compares the interfacial resistances of graded tape and functionally graded cathodes prepared using other methods [15,16,18–20]. Clearly, the functionally graded cathodes fabricated by tape casting technique display much smaller electrode polarization resistances than those prepared by other techniques. At 700 °C, for example, the cathodic polarization resistance for graded tape is only 0.075 Ω cm², compared to 0.21 Ω cm² [15] and 0.74 Ω cm² [18] for another graded cathodes, representing three times to one order of magnitude improvement. The superior electrochemical performance of the functionally graded tape is ascribed to the following reasons. It is believed that LSCF comprised of a fine inner-layer and coarse outer-layer can

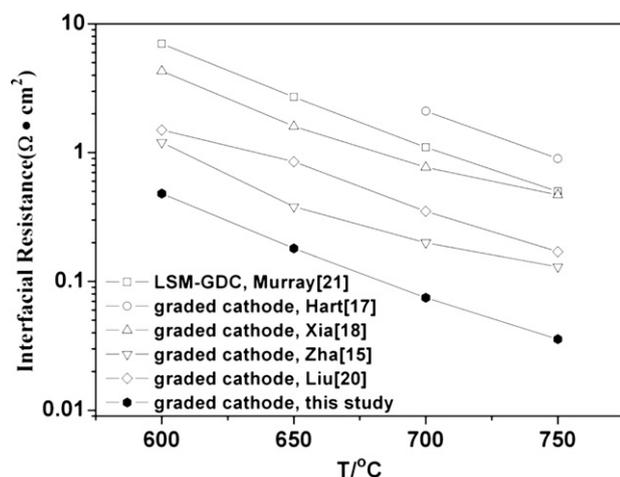


Fig. 5 – Comparison of cathodic polarization resistances of a composite cathode and several graded cathodes prepared using different fabrication processes.

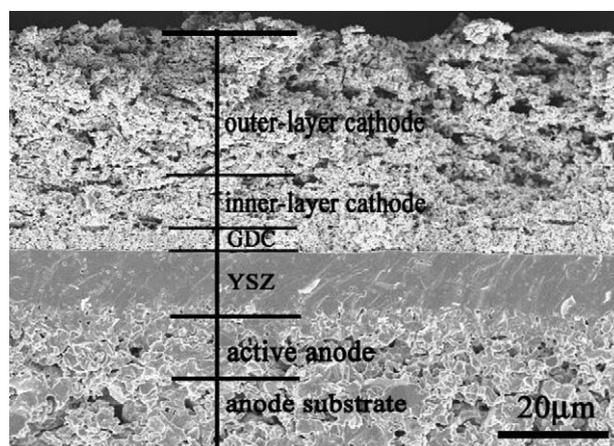


Fig. 6 – A cross-sectional view (SEM image) of an anode-supported single cell with a configuration of LSCF/GDC |YSZ| NiO–YSZ.

reduce electrochemical polarization resistance $R_{p,elchem}$ and diffusion polarization resistance $R_{p,diff}$, respectively [31].

The performance of the graded LSCF cathode was further evaluated in anode-supported cells. In order to avoid the reaction between YSZ and LSCF, a GDC buffer layer, fabricated by a slurry coating process, was introduced between YSZ and LSCF tape. The LSCF tape was directly put on the surface of a GDC buffer layer, followed by co-firing at 1050 °C for 2 h to form a single cell. A cross-sectional view of the anode-supported cell is shown in Fig. 6.

Fig. 7 shows the cell voltages and power densities as a function of current density for anode-supported cells with graded cathode fabricated by tape casting. Peak power densities of 371.5, 744.6, and 1075.3 mW/cm² are demonstrated at 700, 750, and 800 °C, respectively, which are higher than those reported elsewhere under similar conditions [20]. Compared to other fabrication process, such as screen printing [33] and spray process [34] which have been applied to fabrication of porous layer, tape casting can easily control the thickness and morphology of porous electrodes at low cost.

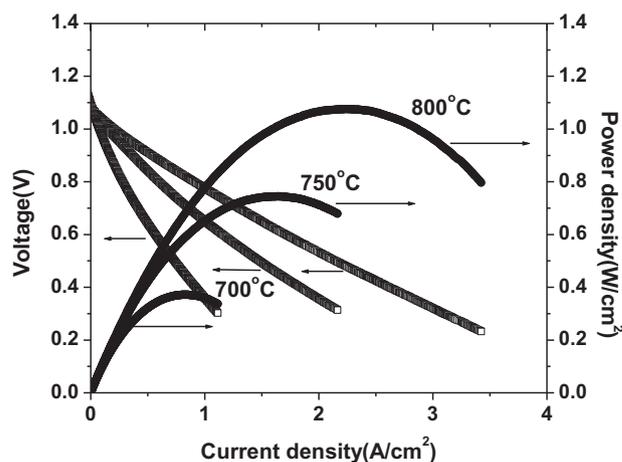


Fig. 7 – Current–voltage (I – V) and current–power (I – P) curves of an anode-supported single cell with graded LSCF cathode tested at 700–800 °C using humidified hydrogen as the fuel and ambient air as the oxidant.

4. Conclusions

Both single layer and graded LSCF cathodes were successfully fabricated by a tape casting process. Compared to single layer LSCF cathode, the graded cathode showed improved electrochemical performance due to the functionally-graded microstructure of the LSCF cathode: finer inner LSCF layer for electrochemical reaction and coarse outer-layer for current collection and gas transport. Sintering temperature has significant effects on the microstructures of the graded cathode and therefore on their electrochemical performance. Low interfacial polarization resistance of $0.036 \Omega \text{ cm}^2$ at 750°C was achieved in GDC-based symmetrical cells when the functionally graded LSCF cathode was fired at 1050°C for 2 h. With graded LSCF cathodes on anode-supported YSZ-based cells, excellent performances were achieved at $700\text{--}800^\circ\text{C}$. The results suggest that the performance of conventional cathodes can be considerably improved by microstructure optimization and the tape casting process has potential to further reduce the fabrication cost of SOFCs.

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REFERENCES

- [1] Liu ML, Lynch ME, Blinn K, Alamgir FM, Choi Y. Rational SOFC material design: new advances and tools. *Mater Today* 2011;14:534–46.
- [2] Zhan ZL, Barnett SA. An octane-fueled solid oxide fuel cell. *Science* 2005;308:844–7.
- [3] Huang YH, Dass RI, Xing ZL, Goodenough JB. Double perovskites as anode materials for solid-oxide fuel cells. *Science* 2006;312:254–7.
- [4] Yang L, Wang SZ, Blinn K, Liu MF, Liu Z, Cheng Z, et al. Enhanced sulfur and coking tolerance of a mixed ion conductor for SOFCs: $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Yb}_x\text{O}_{3-\delta}$. *Science* 2009;326:126–9.
- [5] Yang L, Choi Y, Qin WT, Chen HY, Blinn K, Liu MF, et al. Promotion of water-mediated carbon removal by nanostructured barium oxide/nickel interfaces in solid oxide fuel cells. *Nat Commun* 2011;2:357.
- [6] Liu MF, Choi Y, Yang L, Blinn K, Qin W, Liu P, et al. Direct octane fuel cells: a promising power for transportation. *Nano Energy* 2012;1:448–55.
- [7] Ostergard MJL, Clausen C, Bagger C, Mogensen M. Manganite–zirconia composite cathodes for SOFC: influence of structure and composition. *Electrochim Acta* 1995;40:1971–81.
- [8] Tanner CW, Fung KZ, Virkar AV. The effect of porous composite electrode structure on solid oxide fuel cell performance .1. Theoretical analysis. *J Electrochem Soc* 1997;144:21–30.
- [9] Huijsmans JPP, van Berkel PPF, Christie GM. Intermediate temperature SOFC – a promise for the 21st century. *J Power Sources* 1998;71:107–10.
- [10] Will J, Mitterdorfer A, Kleinlogel C, Perednis D, Gauckler LJ. Fabrication of thin electrolytes for second-generation solid oxide fuel cells. *Solid State Ionics* 2000;131:79–96.
- [11] Shao ZP, Haile SM. A high-performance cathode for the next generation of solid oxide fuel cells. *Nature* 2004;431:170–3.
- [12] Xia CR, Rauch W, Chen FL, Liu ML. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathodes for low-temperature SOFCs. *Solid State Ionics* 2002;149:11–9.
- [13] Fu CJ, Sun KN, Zhang NQ, Chen XB, Zhou DR. Electrochemical characteristics of LSCF-SDC composite cathode for intermediate temperature SOFC. *Electrochim Acta* 2007;52:4589–94.
- [14] Koizumi M. The concept of FGM, functionally gradient materials. *Ceram Trans Am Ceram Soc* 1993;34:3.
- [15] Zha SW, Zhang YL, Liu ML. Functionally graded cathodes fabricated by sol–gel/slurry coating for honeycomb SOFCs. *Solid State Ionics* 2005;176:25–31.
- [16] Hart NT, Brandon NP, Day MJ, Lapena-Rey N. Functionally graded composite cathodes for solid oxide fuel cells. *J Power Sources* 2002;106:42–50.
- [17] Hart NT, Brandon NP, Day MJ, Shemilt JE. Functionally graded cathodes for solid oxide fuel cells. *J Mater Sci* 2001;36:1077–85.
- [18] Xia CR, Rauch W, Wellborn W, Liu ML. Functionally graded cathodes for honeycomb solid oxide fuel cells. *Electrochem Solid-State Lett* 2002;5:A217–20.
- [19] Xu XY, Xia CR, Mao GL, Peng D. Fabrication and performance of functionally graded cathodes for IT-SOFCs based on doped ceria electrolytes. *Solid State Ionics* 2005;176:1513–20.
- [20] Murray EP, Barnett SA. (La, Sr) MnO_3 –(Ce, Gd) O_{2-x} composite cathodes for solid oxide fuel cells. *Solid State Ionics* 2001;143:265–73.
- [21] Liu Y, Compson C, Liu ML. Nanostructured and functionally graded cathodes for intermediate temperature solid oxide fuel cells. *J Power Sources* 2004;138:194–8.
- [22] Ni M, Leung MKH, Leung DYC. Micro-scale modelling of solid oxide fuel cells with micro-structurally graded electrodes. *J Power Sources* 2007;168:369–78.
- [23] Williford RE, Singh P. Engineered cathodes for high performance SOFCs. *J Power Sources* 2004;128:45–53.
- [24] Sahibzada M, Benson SJ, Rudkin RA, Kilner JA. Pd-promoted $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathodes. *Solid State Ionics* 1998;115:285–90.
- [25] Jiang SP. A comparison of O_2 reduction reactions on porous (La, Sr) MnO_3 and (La, Sr)(Co, Fe) O_3 electrodes. *Solid State Ionics* 2002;146:1–22.
- [26] Murray EP, Sever MJ, Barnett SA. Electrochemical performance of (La, Sr)(Co, Fe) O_3 –(Ce, Gd) O_3 composite cathodes. *Solid State Ionics* 2002;148:27–34.
- [27] Yang L, Liu Z, Wang S, Choi Y, Zuo C, Liu M. A mixed proton, oxygen ion, and electron conducting cathode for SOFCs based on oxide proton conductors. *J Power Sources* 2010;195:471–4.
- [28] Adler SB, Lane JA, Steele BCH. Electrode kinetics of porous mixed-conducting oxygen electrodes. *J Electrochem Soc* 1996;143:3554–64.
- [29] Adler SB. Mechanism and kinetics of oxygen reduction on porous $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ electrodes. *Solid State Ionics* 1998;111:125–34.
- [30] Nie L, Liu Z, Liu MF, Yang L, Zhang Y, Liu ML. 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. *J Electrochem Sci Tech* 2010;1:50–6.

- [31] Liu Z, Han MF, Miao WT. Preparation and characterization of graded cathode $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. *J Power Sources* 2007; 173:837–41.
- [32] Liu MF, Dong DH, Peng RR, Gao JF, Juan DW, Liu XQ, et al. YSZ-based SOFC with modified electrode/electrolyte interfaces for operating at temperature lower than 650 °C. *J Power Sources* 2008;180:215–20.
- [33] Lee S, Lim Y, Lee EA, Hwang HJ, Moon JW. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LBCF) cathodes prepared by combined citrate-EDTA method for IT-SOFCs. *J Power Sources* 2006;157:848–54.
- [34] Taniguchi I, van Landschoot RC, Schoonman J. Fabrication of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ thin films by electrostatic spray deposition. *Solid State Ionics* 2003;156:1–13.