

Review

Preparation and characterization of graded cathode $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$

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Abstract

Perovskite oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428), a wonderful electronic–ionic conductor could be used as cathode of solid oxide fuel cell (SOFC). Graded cathode with coarse layer and fine layer, could improve the diffusion rate and electrochemical reaction activity of oxidant. The fabrication and properties of graded LSCF6428 cathode were discussed in this paper. First, pure perovskite LSCF6428 powders were prepared by citrate–EDTA method (CEM), citrate method (CM) and solid phase synthesis (SPS). The powders with higher specific surface area and smaller grain size are easier to be sintered and densified. Single LSCF6428 cathode with thickness of 30 μm was prepared by SPS powders, the porosity of cathode was high about 30% and pore size was about 5 μm . Graded LSCF6428 cathode including 30 μm outer layer and 10 μm inner layer was prepared by SPS and CM powders, respectively. Clear double-layer cathode was observed by SEM, which combined tightly and transitioned gradually. Porosity of outer layer is high about 30% and pore size is about 1–5 μm ; inner layer is finer and pore size is about 0.2–1 μm . Based on the above research, 300 μm yttria stabilized zirconia (YSZ) electrolyte supported cell with single LSCF6428 cathode and double-layer LSCF6428 cathode were prepared, and the properties of two type cells were tested in H_2 . Power density of graded cell is 197 mW cm^{-2} at 950 $^\circ\text{C}$, and improved about 46% comparing that of single layer LSCF6428 cell (135 mW cm^{-2}).

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Keywords: Solid oxide fuel cell; LSCF6428; Graded cathode

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1. Introduction

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) perovskite (ABO_3) composite oxides have high electronic and ionic conductivities and excellent catalytic activity, which can be used as oxygen permeate membrane, catalyst carrier and sorbing material. They are also the good candidates as cathode materials for solid oxide fuel cells (SOFCs), concerned by researchers in SOFC [1]. They are mixed ionic and electronic conductor for containing variable valent cation and doped heterovalent ions. Meanwhile the electronic conductivity of LSCF is 1×10^2 to $1 \times 10^3 \text{ S cm}^{-1}$ and ionic conductivity is about $1 \times 10^{-1} \text{ S cm}^{-1}$ at 800°C [2]. Teraoka et al. [3] investigated ionic and electronic conductivity of LSCF by four-probe method and oxygen permeation technology. As a result, the ionic conductivity increases with the increasing of Sr content, and decreases with the increasing of Fe content.

LSCF could be used as cathode of medium-temperature (IT) CeO_2 electrolyte SOFC at $500\text{--}700^\circ\text{C}$ [4]. Steele and co-workers [5,6] have focused on the development of new cathodes appropriated for IT-SOFCs and LSCF cathodes have been optimized for using with CeO_2 -based electrolytes. Dusatre and Kilner [7] indicated that 70% $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428)–30% $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (GDC) (weight composition) had the best property when GDC electrolyte was used. Although electrochemical properties of LSCF are well, their thermal expansion coefficients (TECs) are quite different from electrolyte. As a result, the electrodes are easily pull-off for long-time operation and thermal cycles, which affects the cell life. In LSCF system, the electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ increased from 87 to 333 S cm^{-1} with the increasing of Sr^{2+} ($x=0.2\text{--}0.4$) at 800°C , but the TEC also increased from 14.8×10^{-6} to $17.5 \times 10^{-6} \text{ K}^{-1}$ ($30\text{--}1000^\circ\text{C}$) [8]. Doped Ca^{2+} LSCF can reduce the TEC of LSCF system [9]. Perry Murray et al. [10] indicated that the TEC of LSCF contained high Fe was lower than that of high Co, and LSCF of high Fe matched YSZ and doped CeO_2 electrolytes easily. So the LSCF6428 contained high Fe (TEC: $13.8 \times 10^{-6} \text{ K}^{-1}$ [11]) much easier matches with yttria stabilized zirconia (YSZ) electrolyte (TEC: $10.78 \times 10^{-6} \text{ K}^{-1}$ [12]).

For achieving TECs match, fine interfacial condition and electrochemical performance between electrolyte and cathode, functionally graded materials (FGM) have been employed to join novel materials or to achieve unique properties [13]. Ideally, the best structure for a functional cathode in SOFC should be the one with both compositional gradient and porosity gradient, consisting of fine grains (and high surface area) close to the electrode/electrolyte surface, and large grains (and thus large pore size) at air/oxygen side [14]. The fine activation layer could efficiently improve the property of SOFC, so, it is necessary to investigate the activation layer cathode near the electrolyte.

In this paper, functionally graded LSCF6428 cathodes were developed for SOFC based on YSZ electrolyte. LSCF6428 powders were fabricated by different methods, and sintering and ceramic properties were investigated, finally single and graded cathode SOFC were tested and discussed.

2. Experimental

2.1. Powder fabrication

Citrate–EDTA method (CEM): LSCF6428 was synthesized by stoichiometric of nitrates of lanthanum, strontium, cobalt and iron ($\text{La}(\text{NO}_3)_3$, 99%; $\text{Sr}(\text{NO}_3)_2$, 99.5%; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%; and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5%), dissolved in distilled water. Ethylenediamine tetraacetic acid (EDTA), which was dissolved by ammonia, and citric acid (total metal ion:EDTA: citric acid (mol ratio) = 1:1.5:1) was added to a thoroughly stirred solution. The mixed solution ($\text{pH} \approx 6$) was evaporated at 80°C , transited to collosol, finally to gelatum. The precursor was dried in oven at 120°C and processed in furnace at different temperature.

Citrate method (CM): The above nitrates were used as starting materials, dissolved in the correct stoichiometric proportion in distilled water. The nitrate solution was then dropped to a thoroughly stirred citrate solution with an excess of 1.5 in total metal ion. The mixed solution ($\text{pH} \approx 7\text{--}9$) was evaporated at $50\text{--}80^\circ\text{C}$, then transited to collosol, finally to gelatum. The precursor was dried in oven at $120\text{--}160^\circ\text{C}$ and processed in furnace at different temperature.

Solid phase synthesis (SPS): Composition LSCF6428 was synthesized by solid state reaction of strontium carbonate and the oxides of lanthanum, cobalt and iron (SrCO_3 , 97%; La_2O_3 , 99.99%; Co_2O_3 , 99%; Fe_2O_3 , 99.99%). La_2O_3 was dehydrated at 1100°C for 4 h before used. The batch powders were thoroughly milled with alcohol for 15 h, dried and calcined at 1100°C , then remilled for 10 h and sieved (400 meshes).

2.2. Characterization of powder

The perovskite phase was determined by X-ray diffraction (XRD) analysis using a D/Max-RC ray diffractometer with $\text{Cu K}\alpha$ radiation. The microstructure of powder was observed by TEM (H-8100 Transmission Electron Microscope, Japanese). The powder was dry-pressed at 200 MPa, and $\Phi 20$ mm disc was sintered at $800\text{--}1100^\circ\text{C}$. Shrinkage ratios of different powders were measured. Density of the samples was determined by Archimedes immersion method. The grain size and microstructure were observed by SEM (JEOL JSM6700, Japanese).

2.3. Characterization of single cell

Single LSCF6428 cathode cell: LSCF6428 powders made by SPS process were wet-coated on counter plate of YSZ ($\sim 300 \mu\text{m}$ thickness, sintered by 1300°C for 10 h [15])/Ni-YSZ ($20 \mu\text{m}$ thickness, 1300°C for 2 h).

Graded LSCF6428 cathode cell: LSCF6428 powders made by CM process were wet-coated on counter plate of YSZ/Ni-YSZ (the same as single cathode cell) as the active layer, in which the thickness is $10 \mu\text{m}$. Thirty micrometer LSCF6428 outer layer made by SPS process (LSCF6428 powders: addition = 10:1, wt.%) was wet-coated on LSCF6428 inner layer. The two types of cathode of cells were sintered at 1150°C for 2 h. Single cells were tested by Arbin BT2000 potentiostat–galvanostat electrochemical testing system. A 97% $\text{H}_2\text{--}3\%$ H_2O gas mixture

was flowed to the anode at 0.2 L min^{-1} , and air to the cathode at 0.3 L min^{-1} . At least two samples of each cathode composition were analyzed to verify cell performances.

3. Result and discussion

3.1. Powders properties

The LSCF6428 powders made by CM and CEM processes were sintered at 800°C for 2 h [16,17]. The powder made by solid phase synthesis was sintered at 1100°C for 2 h [18]. The XRD patterns of three powders are shown in Fig. 1. All of the three powders are pure perovskite phase. The peaks are sharp and strong enough to confirm the high crystallinity. Based on Sherrer formula (1), grain sizes of CEM, CM and SPS were 18.03, 21.98 and 25.89 nm, respectively:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the grain diameter (nm), K is 0.89, λ is the wavelength of X-ray (Cu $K\alpha$ radiation is 0.15406 nm), β is the maximum half-width (rad), and θ is the diffraction angle ($^\circ$).

Grain sizes of three powders are all nanometer class. The sintering temperature of CEM and CM powders are lower than SPS, so grain sizes of CEM and CM powders are smaller than that of SPS powders. The microstructure of CM powders (TEM) is shown in Fig. 2. The grains are spheric and uniform, and grain sizes are 30–60 nm.

3.2. Sintering properties

Green bodies of three powders by dry-pressed were sintered at 1200°C for 2–4 h. Powder grain sizes, shrinkage ratios and ceramic densities are shown in Fig. 3.

The powders with higher specific surface area and smaller grain size are easier to be sintered and densified. As shown in Fig. 3, the grain size of SPS powder is 25.89 nm, both the shrinkage ratio of 8% and density of 4.66 g cm^{-2} are low. On the other hand, the grain size of CEM powder is 18.03 nm, both the shrinkage ratio of 14% and density of 5.58 g cm^{-2} are high. Because different grain size powders have different sintering properties, the SPS and CM powders were selected to prepare the different cathodes in SOFC.

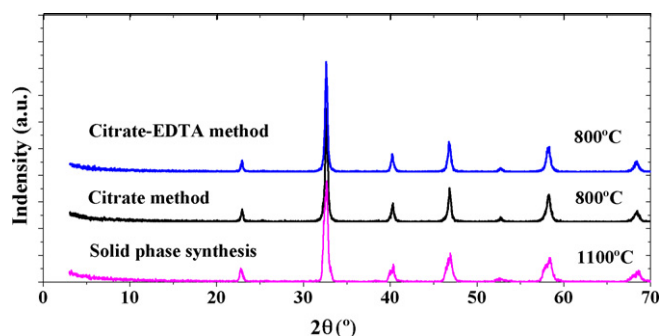


Fig. 1. XRD spectrum of LSCF6428 powders.

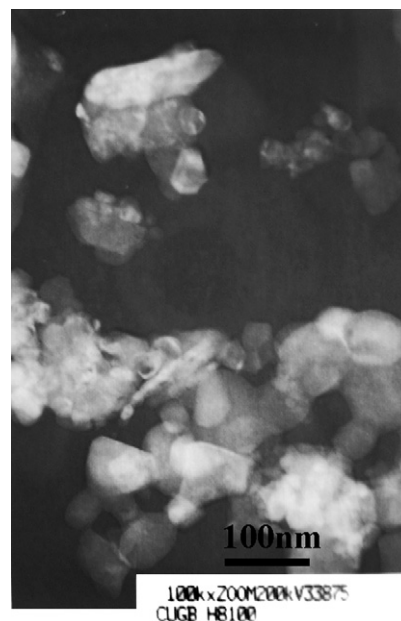


Fig. 2. Microstructure of LSCF6428 powder fabricated by CM process.

3.3. Cell properties of LSCF6428 cathode

Ideal cathode structure should be graded, fine near the electrolyte to minimize activation polarization, and coarse in regions away from the electrolyte to minimize concentration polarization [19]. One of successful effort to improve the performance of LSCF cathodes is microstructure optimization involving graded or double-layer cathode [20].

Fig. 4 indicates that the performance of SOFC with graded cathodes and single cathode. As a result, the power density of graded LSCF6428 cell is 197 mW cm^{-2} at 950°C , which is higher about 46% than that of single layer LSCF6428 cell, which is 135 mW cm^{-2} at 950°C . Area specific resistances (ASR) of graded and single cathode cells are 1.49 and $1.85 \Omega \text{ cm}^2$ (400 mA cm^{-2}) at 950°C , respectively. For the thickness of YSZ electrolyte is about $300 \mu\text{m}$, the electrolyte ASR ($\text{ASR}_{\text{electrolyte}}$) is about $0.375 \Omega \text{ cm}^2$. Meanwhile the anode ASR ($\text{ASR}_{\text{anode}}$) could be ignored for the value is relatively minimum in total ASR ($\text{ASR}_{\text{total}}$). As a result, the cathode ASR ($\text{ASR}_{\text{cathode}}$) of graded layers and single layer are about 1.115 and $1.475 \Omega \text{ cm}^2$, respectively. The $\text{ASR}_{\text{cathode}}$ of graded cathode cell reduced about 32%

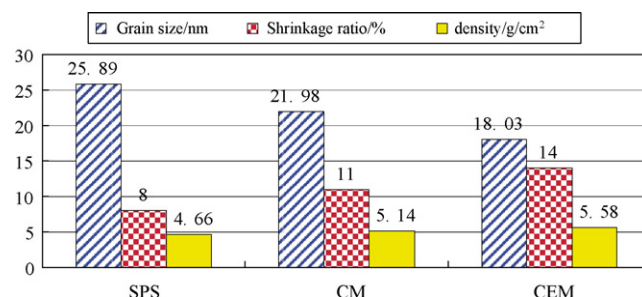


Fig. 3. The powder grain sizes, shrinkage ratios and densities of LSCF6428 for different fabrication methods.

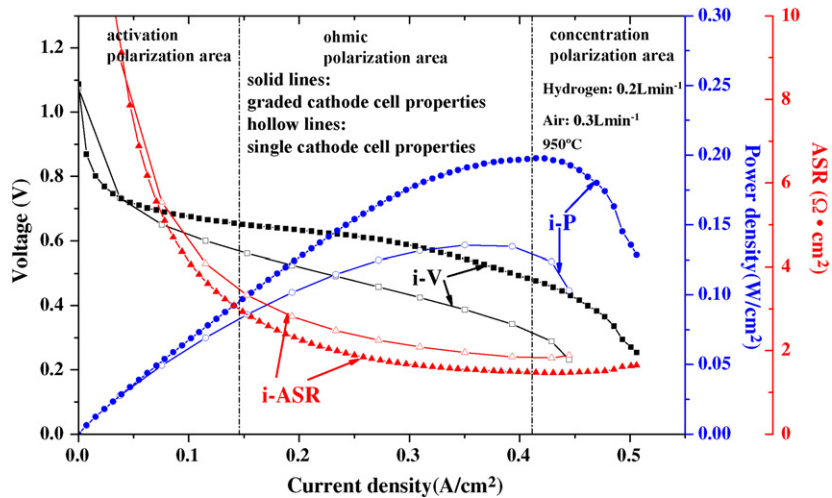


Fig. 4. The properties of graded layer LSCF6428 cell and single layer LSCF6428 cell.

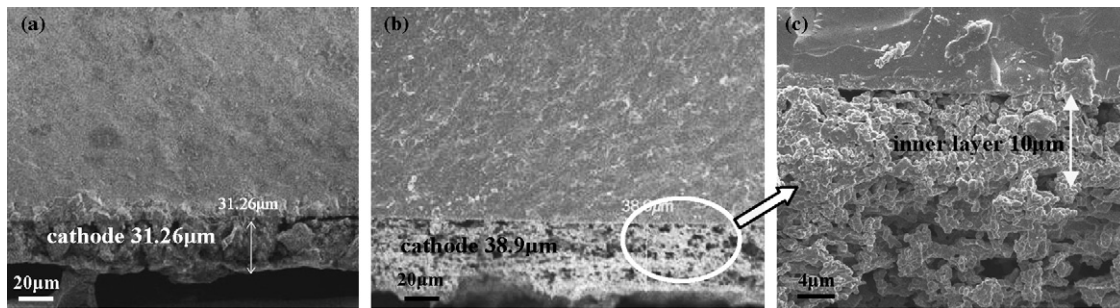


Fig. 5. Micrograph of electrolyte supported cell with LSCF6428 cathode: (a) single layer cathode cell, (b) graded cathode cell and (c) graded cathode cell.

than that of single cathode cell. Meanwhile the activation polarization area in Fig. 4 shows that the voltage of graded cathode cell decreases slower with the current density increasing than that of single cathode cell.

On the other hand, the ASR_{cathode} should increase with the thickness of cathode increasing, but the ASR_{cathode} decreases with the 10 μm activation layer added. So, activation polarization of cathode has great effect on the property of cathode. The activation layer near the electrolyte efficiently decreases the activation polarization of cathode in SOFC.

The single-layer and graded layer cathode cells were observed by SEM. Fig. 5a shows that the thickness of single cathode is 31.26 μm , porosity is high, about 30%, and pore size is about 5 μm . Fig. 5b shows that the thickness of graded cathode is 38.90 μm , in which the inner layer is about 10.00 μm , as shown in Fig. 5c. Both Fig. 5b and c shows that clear graded layer cathode combines tightly and transits gradually. Pore of inner layer is fine, the pore size is about 0.2–1 μm , in which the fine three-phase boundary (TPB) can reduce activation polarization, improve the charge transfer process. Porosity of outer layer is high, about 30%, and pore size is about 1–5 μm , which is benefit to gas transfer and reduce concentration polarization. Finally, graded cathode including fine inner layer and coarse outer layer can reduce diffusion polarization resistance $R_{p,\text{diff}}$ and electrochemical polarization resistance $R_{p,\text{elchem}}$.

4. Conclusion

- (1) Pure perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ powders were prepared by citrate–EDTA method, citrate method and solid phase synthesis. The grain sizes are 18.03, 21.98 and 25.89 nm, respectively.
- (2) For different powders processes, shrinkage ratio and density gradually increased with the grain size decreasing. The powders with higher specific surface area and smaller grain size are easier to be sintered and densified. Fine powders can be used as activation layer and coarse powders can be used as outer layer in cathode of SOFC.
- (3) Power density of graded cell is 197 mW cm^{-2} at 950°C in H_2 , which is improved about 46% than that of single layer LSCF6428 cell (135 mW cm^{-2}). ASR_{cathode} of graded and single cathode cell are about 1.115 and $1.475 \Omega \text{ cm}^2$, respectively, the ASR_{cathode} of graded cathode cell reduced about 32% because of 10 μm active layer added.

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