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Preparation and characterization of graded SSC–SDC MIEC cathode for low-temperature solid oxide fuel cells

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Abstract

Mixed ionic/electronic conductor (MIEC) cathodes with graded composition and microstructures have been fabricated using improved spin-coating technique. Two components, $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) and $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC), were utilized to prepare the graded MIEC cathode. Graded microstructures, i.e., a SSC-rich outer layer with large interconnected pores and a SDC-rich inner layer with small interconnected pores, were observed. The corresponding single cell had an increase of 13.3% in maximum power density at operating temperature of 600 °C. The present work suggests that the graded MIEC cathode has great potential in improving performance of solid oxide fuel cells operated at lower temperature.

Keywords: A. Films; B. Porosity; C. Electrical properties; E. Fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) are being considered as great future power generation devices that have high energy conversion efficiencies and environmental friendliness [1]. Concerning SOFCs, one of the most important research goals is to decrease the operating temperature from 1000 °C in present to 600–800 °C, which would invoke many advantages. For example, lower-cost metallic materials such as ferritic stainless steels can be used as interconnects which makes the stack cheaper and more robust. The mechanical properties of the electrode materials can be significantly improved, leading to good long-term stability of the fuel cell system. Besides, the potential for rapid start-up can also be enhanced if the operating temperature is lowered [1–3].

However, the decreased operating temperature, on the other hand, results in a notable deterioration on electrode activity, especially for the cathode [4–6]. Therefore, it is critical to decrease cathodic interfacial polarization resistance at reduced temperatures. One strategy is to develop a mixed ionic/electronic conductor (MIEC) cathode [7]. The MIEC materials extend the oxygen reduction site from cathode–electrolyte–gas phase to the entire cathode–gas phase interface, which brings a substantial increase in the cathode performance at reduced temperatures.

An electrochemical model has shown that a graded composition could further enhance the electrochemical properties of MIEC cathodes [8]. In the graded cathodes, the outer layer is rich in electronic material to facilitate the current collection well, and the inner layer near the electrolyte is rich in ionic material to favor ionic conduction well. Also it is expected that the graded composition can improve the mechanical properties of the cell due to the reduction in the thermal expansion coefficient mismatch between the electrode and electrolyte materials. Besides, graded porosity in cathode with porous outer-layer and less porous inner-layer, could improve the diffusion rate and electrochemical reaction activity of oxidant [9,10].

The graded cathodes have been reported, such as LSM-(YSZ + CGO)/LSM/LSM-LSCO/LSCO[11], LSM-GDC/LSM-LSCF-GDC/LSCF-GDC/LSCF [12] and LSM-SDC/LSM-LSC-SDC/LSC-SDC/LSC [13]. These graded cathodes demonstrated lowered interfacial polarization resistances as expected. However, these graded cathodes seem complicated in composition, which may have a negative influence on the cell durability due to diffusion at working temperature.

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Table 1
The composition of slurries.

	Composition of powders (wt.%)		The ratio of composite powders to ethyl cellulose (wt.%)
	SSC	SDC	
Slurry-1	50	50	18:2
Slurry-2	70	30	17:3

In this paper, only two components, $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) which is predominantly ionic conducting at low temperature and $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) [14] which is mixed ionic/electronic conducting, were selected in the present MIEC cathode. The conductivity character of cathode film was modulated by the ratio of SSC and SDC. In our previous work, spin-coating technique was proved to be an effective method to fabricate nanostructured porous thin SSC–SDC cathode with high electrochemical performance [15]. Presently, the SSC–SDC film with graded composition and porosity was designed to further promote cell performance. Single cell with a porous Ni/SDC cermet as anode and a dense SDC as electrode was assembled, and the cells was tested at a low temperature of 600 °C in comparison with a cell with non-graded cathode. The contribution of the graded MIEC cathode was discussed.

2. Experimental procedure

2.1. SSC and SDC powder synthesis

Glycine-nitrate process (GNP) was used to synthesize SSC and SDC powders [16]. Stoichiometric amounts of the precursors $Sm(NO_3)_3·6H_2O$ (A.R.), $Sr(NO_3)_3$ (A.R.), and $Co(NO_3)_2·6H_2O$ (A.R.) were dissolved in deionized water. Then glycine (NH_2CH_2COOH) was slowly added to the metal nitrate aqueous solution under constant stirring. The molar ratio of NO_3^- to glycine was 2. The resulting solution was then heated and concentrated to about 2 mol l^{-1} on the metal nitrate basis. While the solution is still hot, it was added dropwise to a beaker which was preheated to 300–400 °C. Spontaneous ignition occurred, and a voluminous, black, sponge-like SSC ash was obtained. The SSC ash was subsequently fired at 700 °C for 4 h to remove residual carbon and get the SSC powders eventually. The SDC powders and NiO-SDC powders were prepared using a similar procedure. SSC powders were mixed with SDC powders correspondingly by wet ball-milling for 36 h as the cathode material.

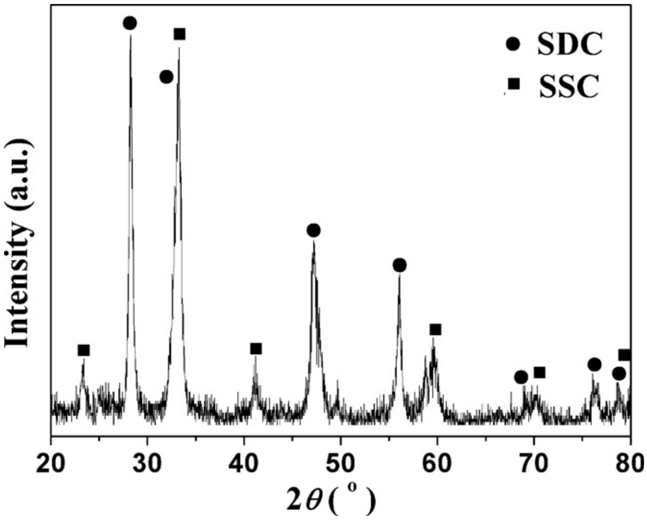

Fig. 1. XRD patterns of graded cathode film after electrochemical test.

2.2. Cathode and cell fabrication

An anode-support single cell structure was adopted. NiO-SDC powders were first pressed at 100 MPa into a disc

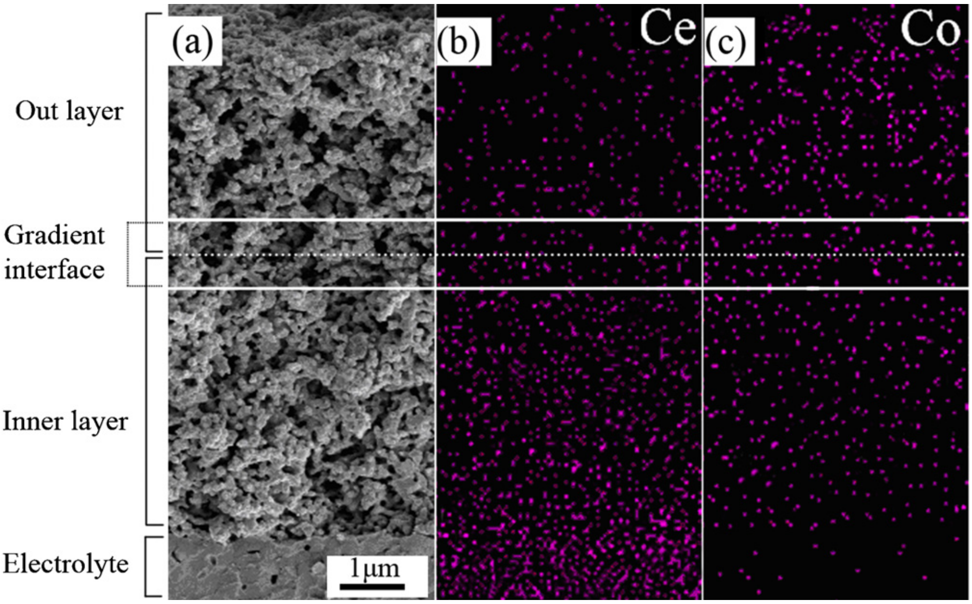

Fig. 2. SEM micrograph of cross-sectional view of the graded cathode, and Ce and Co EDS dot mappings of the cross-section.

(~15 mm in diameter and 1 mm in thickness). Then SDC powders was placed on the disc and pressed at 200 MPa to yield a bilayer disc. The bilayer was subsequently fired at 1350 °C for 4 h and reduced in flowing H_2 at 600 °C for 4 h [15].

Two cathode slurries with different content of SSC and SDC powders, ethyl cellulose were prepared in this work as shown in Table 1, ethyl cellulose acted as both pore-forming and viscosity-adjusting agent. Ethanol was used as the media.

Slurry-1 was first used to spin coated onto the electrolyte surface. The slurry was dropped onto the electrolyte with a spinning speed at 6000 rpm for 30 s. The inner layer (~7.5 μm, after sintering) was deposited with 50 drops (about 2.5 ml) of slurry-1. Then slurry-2 was subsequently coated on to the inner layer with the same spinning speed and times. To avoid cracks or pores induced by evaporation or decomposition of the organics during the following co-sintering step, the inner layer was heated at 400 °C for 10 min with a heating rate of 10 °C min^{-1} and a cooling rate of 20 °C min^{-1} before spin coating the outer layer [17]. Finally, the spin-coated films on electrolyte/anode bilayer substrate were sintered at 950 °C to get porous cathodes. Furthermore, slurry-2 was used to fabricate a reference cell with non-graded cathode. The reference cathode was deposited with 100 drops of slurry-2 with the same spinning speed and time and subsequently sintered at 950 °C.

2.3. Cell testing

Three of each type cells were tested at 600 °C using humidified (3% H_2O) H_2 as fuel gas and the cathode was fed with air as oxidant. Current density–voltage (I–V) relationship was determined for the cells using a potentiostat (CHI600C, CH Instruments) with a constant fuel flow rate of 60 cm^3 min^{-1}. The phase of the cathode film after electrochemical test was identified using X-ray diffraction. The microstructure of the electrodes was observed using a field emission scanning electron microscope (FESEM, model

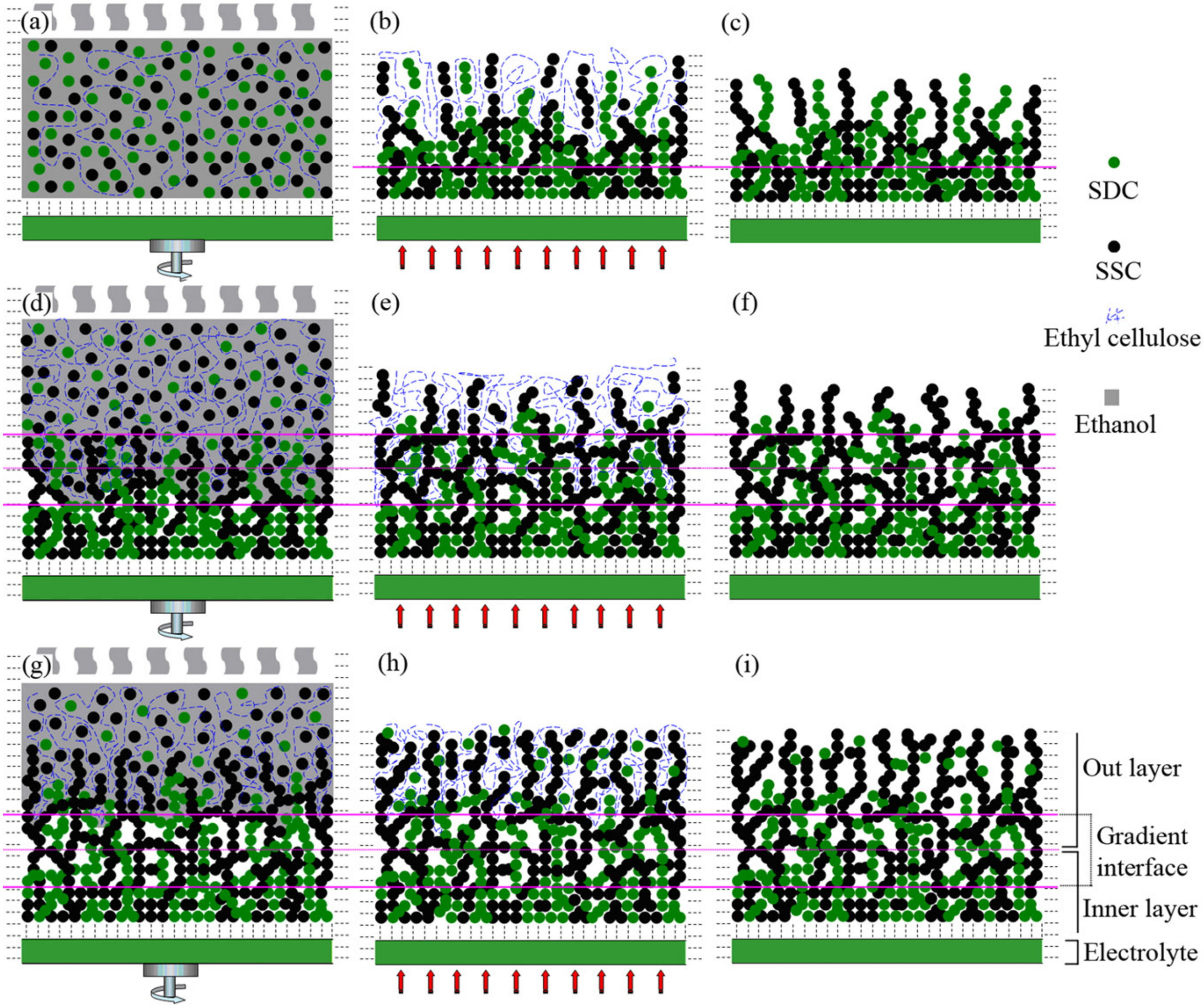

Fig. 3. Schematic illustration of graded SSC–SDC composite MIEC cathode by spin-coating method: (a–c) the formation of inner layer, (d–f) the formation of gradient interface, and (g–i) the formation of outer layer.

Table 2
The contents of elements in the bilayer film by spin coating and after sintering at 950 °C in the air.

	Contents of elements (wt.%)			
	Ce	Co	Sr	Sm
Outer-layer				
Observed	28	21	16	35
Precursor	24	23	17	36
Inner-layer				
Observed	37	18	12	33
Precursor	40	16	12	32

SIRION-100, FEI). The element distribution was studied using an energy-dispersive spectroscopy (EDS) attachment and quantified through image analysis software (DT-2000 image analysis system).

3. Results and discussion

As shown in Fig. 1, the cathode after electrochemical test only contained SDC and SSC phases. It indicates that the cathode is stable in chemical composition.

EDS analysis results (Table 2) present the evolution in composition is in agreement with that of the designed two layers, SSC(Co)-rich outer layer and SDC(Ce)-rich inner layer. Considering no reactions between SSC and SDC, it is comprehensible that the composition of layer follows the ratio of powders in slurry on the whole, i.e., higher SDC content in slurry-1 led to higher SDC content in inner layer, while higher SSC content in slurry-2 led to higher SSC content in outer layer (Fig. 2).

Nevertheless, there are slight deviations of contents of elements in the outer layer and inner layer between the designed precursory slurry (Table 2). That might caused by the mixed component area formed on the verges of boundary.

The EDS dot mapping of the resulting cathode (Fig. 2b and c) shows that the Ce content gradually increased from the outer layer to the electrolyte, while the Co distribution exhibited an opposite trend as designed. No sudden changes of elements content appeared at the boundary of two layers, which is due to the infiltration of slurry-2 into the pores of inner layer surface resulted from the decomposition of ethyl cellulose after 400 °C heat treatments (Fig. 3d–f).

The two layers are actually nanostructured as shown in Fig. 3. The porous structure was constructed by the SSC and SDC particles whose size is in the range of 200 nm. This structure can offer extremely high surface area for oxygen reduction. Meanwhile, the large interconnected pores in outer layer (Fig. 3a), shaped by the decomposition of more ethyl cellulose after heat treatments (Fig. 3h and i), facilitate oxygen mass transport. Fine agglomerate and small interconnected pores in inner layer (Fig. 3b) make triple boundaries much longer, providing large areas where electrochemical reaction could take place.

Different from those graded structures fabricated by CVD, spray painting or sputtering deposition, where the defects of pore structure are, usually, easily observed between each layer [18], the graded structure fabricated by spin-coating shows a continuous and uniform pore structure at the cross-section, which means that the two layers joint well (Figs. 2a and 4c). As mentioned above, it could also be attributed to the infiltration of slurry-2 into the pores of inner layer surface (Fig. 3d–f).

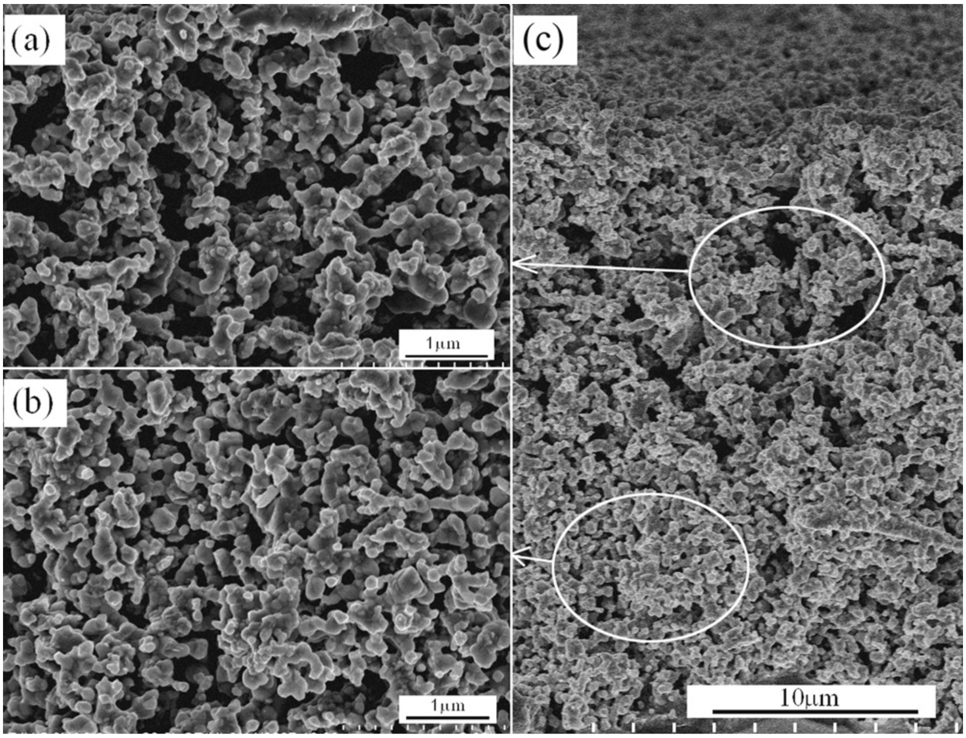

Fig. 4. SEM micrographs of the two layers in the graded cathode: (a) outer layer and (b) inner layer.

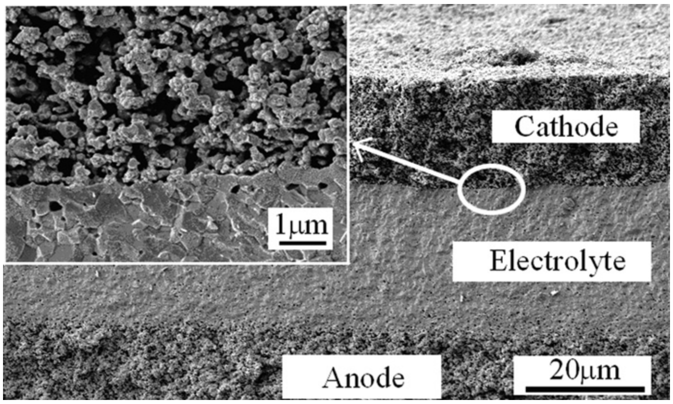

Fig. 5. SEM micrograph of the whole cell cross-section.

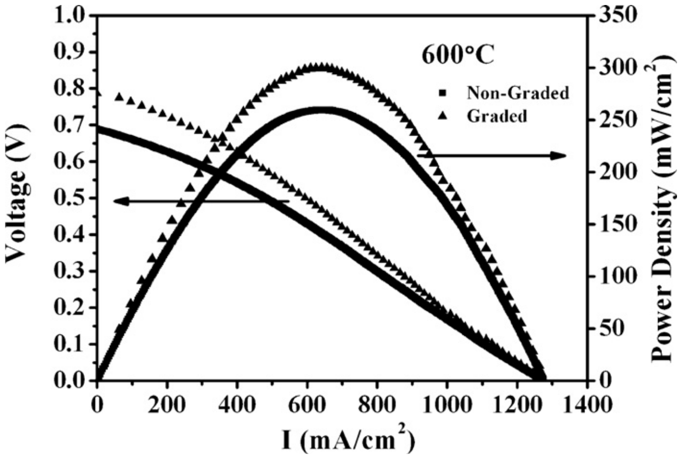

Fig. 6. Cell voltages and power densities as a function of current density for a single cell with graded cathode and without graded cathode.

In addition, the SEM micrograph of the whole cell cross-section (Fig. 5) shows that there is no crack at the interface between cathode and electrolyte. It indicates that the grading in composition and porosity also help in decreasing the mismatch at the interface effectively and ensure the mechanical properties of the whole cell eventually.

Fig. 6 shows the cell voltages and power densities at 600 °C as a function of current density for single cells with graded cathode and without graded cathode. The open current voltages (OCVs) are 0.786 V and 0.689 V, respectively. The gap of OCV between practical and theoretical value (1.033 V) is mainly due to electric leak in the electrolyte, because SDC has slight electronic conductivity at 600 °C [19]. In addition, the OCV is also related to the density of the electrolyte. Internal connected pores in the electrolyte film (Fig. 5) lead to a lower OCV [20].

The maximum power densities are 300 mW cm^{-2} and 259 mW cm^{-2}, respectively. Compared to the single cell without graded cathode, the maximum power density has a 13.3% increase.

In this work, the composition and preparation condition in anode and electrolyte are identical for the both cells, it is suggested that their difference in the both cells could be neglected. Thus, the graded cathode could be significant in improving the cell performance. Ni et al. [21] concluded that a maximum increase of 30% could be theoretically expected if a well-graded electrode is constructed utilizing particles sizes and porosity grading. In the present work, the adoption of graded porosity and composition has attained a 13.3% increase. It is considered that the modulation in composition could be more convenient than particle sizes.

4. Conclusions

Graded SSC–SDC MIEC cathode has been successfully fabricated by alternate spin-coating and heat treatment technique. The resulting cathode with two layer structure was graded in composition and porosity. The outer layer had higher SSC content and coarser pores, while the inner layer had higher SDC content and finer pores. A relatively higher voltage and maximum power density was obtained (0.786 V and 300 mW cm^{-2} at 600 °C) for a single cell with the graded cathode. Compared to the single cell without graded cathode, the maximum power density has a 13.3% increase. The promising results demonstrate that the graded MIEC cathode route is an effective way to improve performance of solid oxide fuel cells operated at lower temperature.

Acknowledgments

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