

Preparation and performance optimization of intermediate temperature cathode-supported SOFC

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Abstract. A cathode-supported intermediate temperature solid oxide fuel cell (IT-SOFC) was prepared by the combination of slurry spin-coating and co-sintering. LSC-GDC ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3\text{-(Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$) was used as the cathode, and LSGM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$) prepared by Glycine-nitrate (GNP) method was adopted as the electrolyte. Compared with the conventional SOFC, the electrical performance of the cathode-supported IT-SOFC is increases by 17%.The electrical output performances and the microstructures of the different cathode-supported single cells which were made by adding various pore formers of 15%wt into the cathode were compared. Results indicates that carbon black was the best pore former for the intermediate temperature cathode-supported SOFC. The maximum power density obtained at 800°C is 539mW/cm².

1. Introduction

Solid Oxide Fuel Cell (SOFC) is a conversion device made of full firmware that directly converts chemical energy contained in fuel and oxidant into electrical energy. This emerging technology will meet the rapid growth of the world. The electricity demand and improvement of energy structure have a huge positive impact on global environmental protection [1]. SOFC operation at a low temperature (below 800°C) not only expands the range of material selection and lower the cost, but also avoids the problems of poor stability and compatibility among cell components. Thus, lower operating temperature of SOFC can achieve more stable cell performance [2].

Nowadays, the most studied in the field of SOFC is the traditional Ni-based anode cell with YSZ as the electrolyte, which is simple to be prepared with low cost. However, performance degradation in low-temperature environments has become a huge limiting factor [3, 4]. On one hand, due to the high activation energy of SOFC cathode redox reaction at intermediate temperature, the main polarization loss of the cell originates from the cathode. It is useful to develop cathode materials with high performance at intermediate temperatures [5, 6]. On the other hand, the anodic or cathodic support structure can reduce the ohmic loss of the cell through the thin film of the electrolyte, and hence improve the efficiency of cells.

Some researchers [7] found that the ($\text{La}_{0.75}\text{Sr}_{0.25}$)_{0.95}MnO_{3±δ} LSM-YSZ cathode-supported single cell formed by co-pressing obtained the maximum power density of 419mW/cm² in humidified hydrogen (3% H₂O) fuel atmosphere at 800 °C. Park et al. [8] fired LSC ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$) and GDC ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$) at a high temperature to form LSC-GDC composite cathode with better mixed conductivity and longer three-phase interface (TPB).A maximum power density of over 400mW/cm² in humidified hydrogen at 600 °C was obtained by optimizing the cathode microstructure. Composite cathode-supported cell with good catalytic activity and conductivity cathode was promising in intermediate temperature solid oxide fuel cells (IT-SOFC).



Pore formers can optimize the microstructure of cathode, improve oxygen transport in the cathode layer, increase the specific surface area of the electrode which provide more reactive sites in the electrode and reduce the reaction gas polarization resistance. Accordingly, a good performance of cells has been achieved by using pore formers [9]. Researchers adjusted the principle of the microstructure according to the pores left by the evaporation of the pore former during the firing of electrode. Carbon blacks, polymer microspheres, PMMA and other pore formers were added to the cathode. The cell performance can be improved through the optimization of pore structure of the cathode.

A fuel cell comprising a LSGM electrolyte prepared by the Glycine-nitrate (GNP) method, a Ni-GDC anode, and a LSC-GDC cathode support. Cathode-supported cells were prepared by slurry spin-coating and co-sintering, and their electrical output performances were compared with conventional fuel cells (NiO-YSZ/YSZ/LSM, Ningbo SOFCMAN Energy Co., Ltd., China). The cathodes were modified by different kinds of organic and inorganic pore formers. The microstructure of LSC-GDC cathode-supported cells was characterized to analyze the effects of pore formers on the power generation performance of the cells to optimize the performance of IT-SOFC.

2. Experiment

2.1 Preparation of Electrode and Electrolyte Materials

$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC, 0.5~2 μm , Ningbo SOFCMAN Energy Co., Ltd, China) and $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$ (GDC, 0.5~3 μm , Ningbo SOFCMAN Energy Co., Ltd., China) were mixed at a mass ratio of 6:4. The 5wt% of PVB, appropriate amount of ethanol, 15wt% of carbon black, and flour or PMMA (MP-300, Soken Chemical & Engineering Co., Ltd, Japan) were then added in the mixture. The mixture was ground in an agate mortar for 2 h and mixed evenly. 1.2 g of the mixture after passing through a 120 mesh sieve was uniaxially die-pressed, followed by isostatic pressing at 80MPa, and then obtain a substrate with a diameter of 25 mm and a thickness of 1.2 mm. The substrate was finally placed in a muffle furnace and pre-fired at 1100 °C for 2 h.

$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3.6}$ (LSGM) [10] was prepared by GNP method. A certain amount of SrCO_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were weighed according to the stoichiometric ratio in a beaker dissolved with deionized water. The glycine (glycine: metal ion = 1.5:1) was added and stirred at 80°C for 1 h to prepare a clear and evenly solution, which was evaporated in an oven to remove excess water. Afterwards, the precursor of LSGM was obtained after combustion. The precursor was fired at 1000°C for 2 h and ground to uniform powder after cooled to room temperature in air. Finally, the as-prepared powder was pressed at 80 MPa and placed in the muffle furnace at 1400°C for 4 h to obtain a final electrolyte powder.

2.2 Preparation of Single Cell

The electrolyte slurry was prepared by mixing a small amount of the above-prepared electrolyte powder with 25wt% of binder (ethyl cellulose: α -terpineol = 1:4) and a suitable amount of ethanol. The cathode support substrate was spin-coated homogeneously on a spin coater (KW-4A, SETCAS Electronics Co., Ltd, China), followed by a spin-dry-spin coating cycle three times. A buffer layer of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ thin film between the anode and the electrolyte was obtained by the same way. Finally, the LSC-GDC/LSGM/SDC three-in-one matrix was sintered at 1300°C for 4 h.

NiO and GDC powders with a suitable mass ratio of 6:4 were mechanically mixed with 40wt% of binder (ethylcellulose: α -terpineol = 1:4) and a suitable amount of ethanol. The obtained slurry was coated on the three-in-one matrix where close to the electrolyte to form an anode which had an effective area of 0.785 cm². And then the disk was calcined at 1150°C for 2 h to obtain a final cathode-supported single cell.

2.3 Characterization and Performance Testing

The D/Max 2400 X-ray crystal diffraction was used to characterize the crystal structure and composition of the LSGM (XRD, Rigaku Co., Ltd., Japan). Automatic gas adsorption instrument (Quantachrome Co., Ltd, USA) with nitrogen as adsorption medium was used to examine pore volume, pore distribution and specific surface area. The porosity is equaled to the ratio of the pore

volume and the total volume of the material. The QUANTA 450 scanning electron microscopy (SEM, FEI Co., Ltd, USA) was used to observe the micro morphology of the surface of the cathode sample after adding different pore formers. The single cell was encapsulated with the constructed single-cell reactor [11] by Pt net current collection and glass ring sealing. Electrochemical performance test was performed at intermediate temperature (650-800°C). The nickel oxide of the anode is reduced to nickel by hydrogen reduction in situ at 900°C for 2 h. In the power generation performance tests with hydrogen, the flow rates of H₂ and O₂ were 80 ml/min and 50ml/min, respectively. HV-151 potentiostat constant current instrument was used to adjust the cell current. CH604D (Shanghai Chen Hua Instrument Co., Ltd.) electrochemical operating instrument was employed to measure the cell voltage.

3. Results and Discussion

3.1 XRD Characterization of Electrolyte Materials

The XRD diffraction pattern of the LSGM electrolyte material after calcinations at 1000°C for 2h compared with the standard spectrum of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ} (PDF#54-1231) can be seen in figure 1(a). The location of the characteristic peaks corresponds basically. The peak shape of the sample shows a cubic perovskite structure phase and a slightly miscellaneous peak. It is demonstrate that the pre-sintered LSGM electrolyte material has a large number of perovskite phases, but still exists many miscellaneous phases. Figure 1 (b) shows the XRD diffraction pattern of the LSGM electrolyte material after calcination at 1400 °C for 4h compared with the standard spectrum of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ} (PDF#54-1231). The characteristic peak is symmetrical and sharp with high intensity, basically no miscellaneous peaks. It is demonstrate that the LSGM electrolyte was successfully prepared by GNP method, and had a stable single perovskite structure after sintering at 1400°C for 4 h.

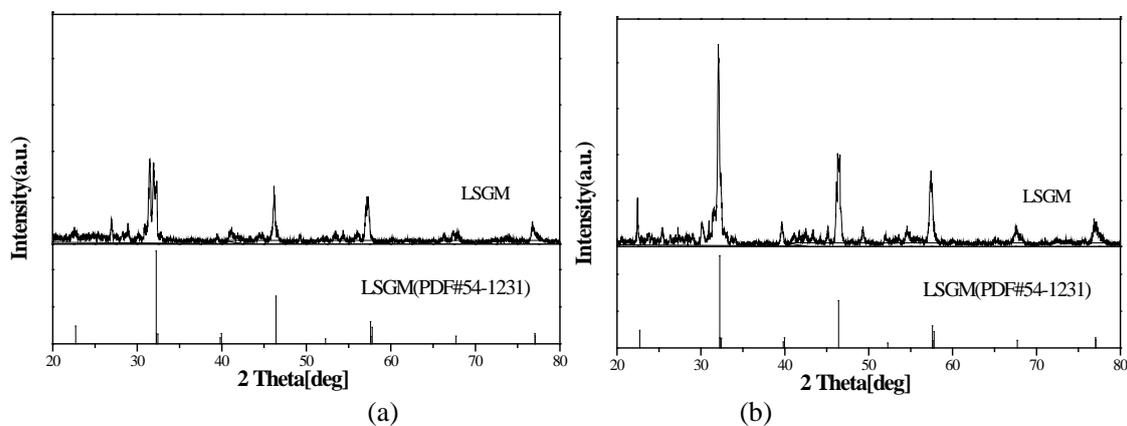


Figure 1. XRD patterns of electrolyte materials at different calcinations temperatures: (a)1000°C (b) 1400°C.

3.2 Comparison of Single Cell Performance

The electrical output performance of cell A and cell B was tested under a hydrogen fuel atmosphere. The electrical output performance curve (I-V-P) is shown in figure 2(a) and figure 2(b). In figure 3(a), the OCV values of the self-made cells are 1.197, 1.194, 1.175, and 1.172V at 800, 750, 700, and 650°C, respectively, which all exceed 1.10 V indicate that the as-prepared LSGM electrolyte spin-coated on the self-made cell substrate is dense and no leakage. Correspondingly, the maximum power density at 800, 750, 700, and 650°C are 507, 333, 221 and 188mW/cm², respectively. Compared with the output performance curve of the conventional single cell in figure 3(b), the OCV of the self-made cell is higher at each temperature. The maximum power density obtained at 800 °C is 17% higher than that of the conventional cell, indicating that the self-prepared LSC-GDC cathode-supported cell has better

electrochemical catalytic activity and better electrical performance than conventional single cell at intermediate temperatures.

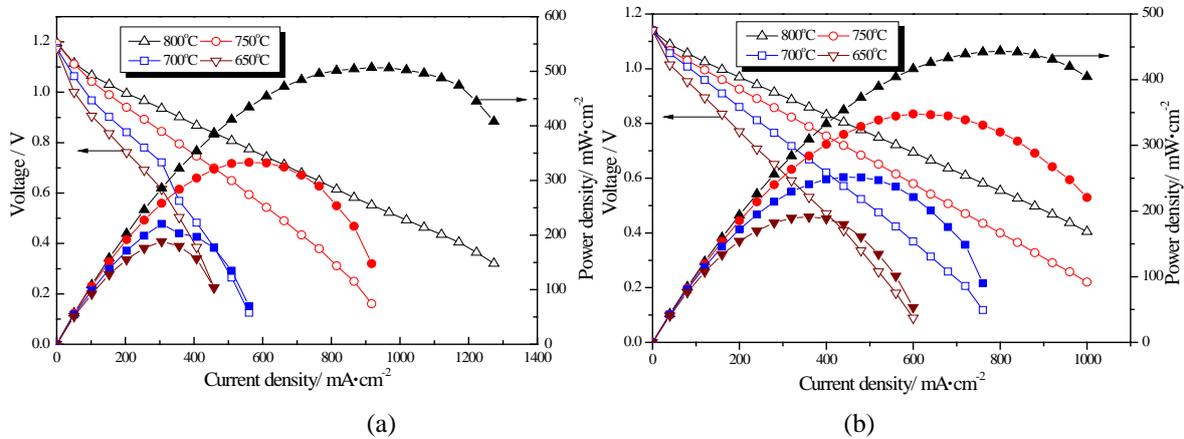


Figure 2. The power generation performance of different single cells: (a) cell A (b) cell B.

3.3 The Influence of Pore Formers on Performance of Single Cell

Figure 3 shows the electrical performance of a single cell (including I-V and I-P curves) with 15wt% of different pore formers added to the composite cathode. It can be seen from the figure that the OCV of each cell is close to the theoretical voltage at each temperatures, which demonstrated that the spin-coated electrolyte is dense and no leakage. Due to the electrochemical activity of the cell electrode material and the influence of the cell polarization, the OCV does not decrease with increasing temperature as compared with the theoretical voltage [12] of the electrochemical reaction of the hydrogen fuel cell.

It can be seen from figure 3(a) (b) (c) that the maximum power densities of cathode-supported cells with carbon black, flour and PMMA were 539, 535 and 410mW/cm², respectively. Compared with the above-mentioned single cell without pore former, the maximum power density at a temperature of 800°C is increased by adding 15wt% of carbon black or flour to the composite cathode. Furthermore, all maximum power densities are obtained at very high current densities, indicating that the addition of pore formers improves the structure of the cathode support and reduces the concentration polarization loss of the cathode, which could result in an improving of cell performance.

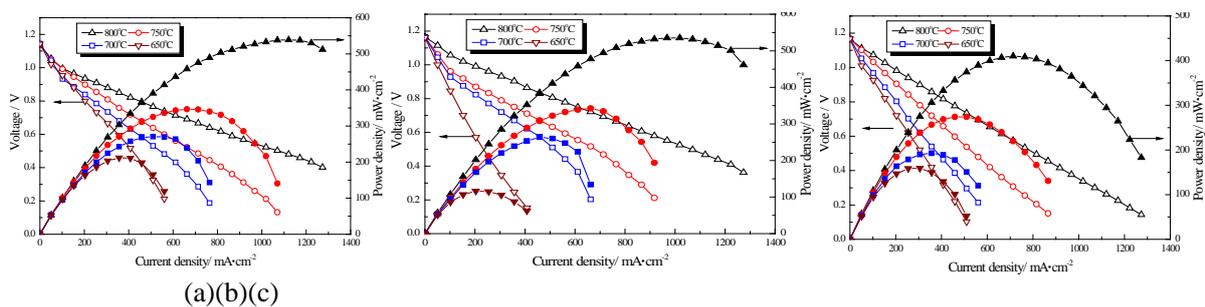


Figure 3. Electrical output performance of single cell in H₂ with different pore formers: (a) carbon black (b) flour (c) PMMA.

3.4 Cathode Characterization of Different Pore Formers

The cathode specific surface area and cathode pore volume of the single cell can be measured by the nitrogen adsorption method to calculate the cathode porosity of the single cell added with different pore formers. According to pre-sintered diameter d_1 and the post-sintered diameter d_2 of the measured cell disk, a sintering shrinkage of $100\% \times (d_2 - d_1) / d_1$ was obtained [13]. Table 1 shows the

comparison of cathode porosity, cathode specific surface area, and sintering shrinkage of single cell with different pore formers. Carbon black and flour as pore former both achieve ideal cathode porosity. The cathode specific surface area of PMMA reaches to $2.134\text{m}^2/\text{g}$. The sintering shrinkage of carbon black as pore former is significantly better than the others, indicating that the carbon black as pore former has better mechanical properties, which cause less susceptible to damage during electrochemical tests.

Figure 4 shows the SEM image of the microstructure of the single cell cathode surface with different pore formers. The LSC particles are attached to the sintered GDC frame work which connected to the network, which is beneficial for the electrochemical catalytic activation of oxygen. it can be seen from figure 4(a)(b)(c) that the pores formed on the surface of the cathode with PMMA and carbon black are evener than that with flour asp reformer. The PMMA used in this experiment was nan-scale, thus, the pore size formed by figure 4(c) is fine and the porosity is low. Although there is a very high specific surface area that can increase the number of reactive sites, the very fine pore size can reduce the countercurrent diffusion of fuel and steam. Therefore, the overall electrochemical reaction rate was limited and the electrochemical performance of a single cell with 15 wt% of PMMA as cathode pore former is reduced, which is not conducive to the improvement of cell performance. Carbon black in Figure 4(a) leaves macro-porous structure of 1 to $10\mu\text{m}$ on the surface of the cathode, and also has a part of macro-porous around $1\mu\text{m}$. This kind of pore distribution with large and small pores improves the reaction and diffusion of the gas in the cathode support and reduces the loss of concentration polarization. The presence of macro-porous increases the reactive sites and improves the cell performance. In summary, carbon black is the most suitable cathode pore former which can effectively improve the microstructure of the cathode and the performance of the cell.

Table 1. Sintering shrinkage of the single cell, porosity and specific surface area of the cathode with different pore formers

| pore formers | Sintering shrinkage | porosity | specific surface area(m^2/g) |
|--------------|---------------------|----------|--|
| carbon black | 19.12% | 36.8% | 1.283 |
| flour | 2.64% | 42.1% | 1.189 |
| PMMA | 3.52% | 23.4% | 2.134 |

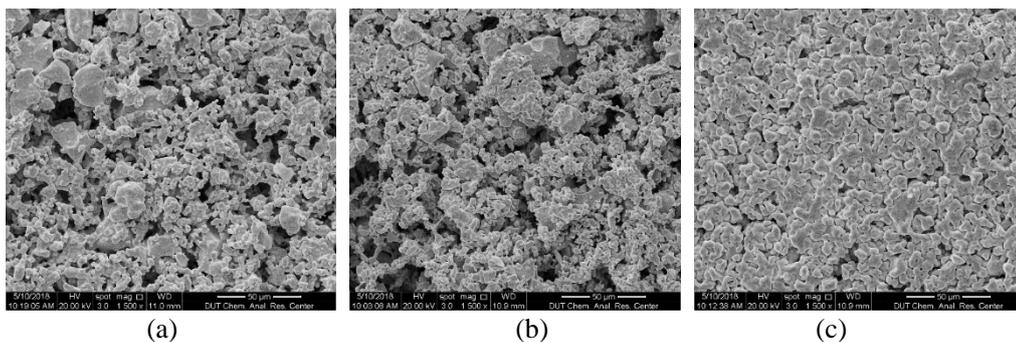


Figure 4. Microstructure of cathode surface of single cell with different pore formers: (a) carbon black; (b) flour; (c) PMMA.

4. Conclusion

A slurry spin-coating combining with co-sintering was adopted to prepare a three-in-one matrix based on a LSC-GDC cathode support and electrolyte layers. The prepared electrolyte LSGM had a stable pure perovskite phase after sintering at 1400°C . Compared with the conventional cell, the cathode-supported cell had better performance at intermediate temperatures. The addition of carbon black enables the cell achieves a high power density of $539\text{mW}/\text{cm}^2$ at 800°C under hydrogen fuel. And the cathode of the cell had rich pore structure, a porosity of 36.8% and a specific surface area of $1.283\text{m}^2/\text{g}$. The cell with carbon black as pore former is easier to sinter compared with flour and

PMMA as pore former, so that it is the best choice to improve the performance of the cell at intermediate temperature.

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