

Study on Performance and Preparation of Lanthanum-Strontium-Iron-Chromium Electrodes for Using in Symmetric SOFC

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Abstract: Solid oxide fuel cells (SOFCs) is a transformative energy conversion technology that offers higher efficiency, reliability and environmental friendliness compared to conventional systems. In this study, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (LSFCr) was prepared by a sol-gel synthesis route and subsequently applied to a symmetric solid oxide fuel cells (SSOFCs). The LSFCr crystal structure was analyzed by X-ray diffraction (XRD) analysis. In order to reduce the manufacturing cost and simplify the cell structure, the SSOFCs configuration LSFCr|SDC|SSZ|SDC|LSFCr (with SDC buffer layer) - was designed using LSTF electrodes, SDC and SSZ electrolytes. The cell has an R_p of $0.7 \Omega \text{ cm}^2$ and a PPD of 200 mW cm^{-2} at 800°C . Notably, the symmetric cell demonstrated robust stability over five redox cycles and maintained performance integrity in short-term durability evaluations, underscoring its potential to advance SSOFCs technology.

Keywords: Symmetric Solid Oxide Fuel Cells; Electrochemical Properties; Fuel Cell; Stability Testing.

1. Introduction

The use of traditional energy sources has led to significant greenhouse gas emissions, exacerbating the problems of global climate change and environmental pollution and posing enormous challenges to human society and the ecosystem. Substituting existing power plants with SOFCs systems has the potential to greatly increase energy efficiency and cut down CO_2 emission. Yet, to lengthen system life time, ongoing development of materials and fabrication process is still needed. The have three key components: the cathode is responsible for reducing oxygen to ions, the electrolyte serves to allow the ions to migrate, and the anode is the place where the fuel gas reacts to produce electrical energy, and this cycle is connected to an external circuit to form a current supply [1-4].

Compared with conventional SOFCs, SSOFCs have fewer sintering steps, simpler structure, lower preparation cost, better thermal cycling performance and excellent redox cycle stability[5]. Therefore, the development of symmetric electrode materials with reliable redox cycle stability effectively solves the problems of carbon accumulation or sulfur poisoning at the anode, which are prone to occur in conventional SOFCs, and the above problems can be solved by changing the cathode and anode inlet air. SSOFCs electrode materials have stable structure and chemistry in oxidizing and reducing atmospheres and have high electrical conductivity and electrochemical catalytic activity towards oxygen and fuel gases[6]. Ruiz-Morales[7] used $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) as cathode and anode, but its electrode performance is relatively low and the redox stability is weak. With the continuous research, more electrodes with chalcogenide structure have been applied to SSOFCs, such as the materials that have been developed such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (LSCrF) [8], $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) [9], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ (LSFS) [10], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [11], $\text{Sm}_{0.7}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Ti}_{0.15}\text{Ru}_{0.05}\text{O}_{3-\delta}$ (SSFTR)[12].

In the above context, we explore the performance of

$\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr) electrode material prepared into a symmetric cell (LSFCr|SDC|SSZ|SDC|LSFCr) with oxidized resistant (Sc_2O_3) stabilized zirconium oxide (ZrO_2), referred to as (SSZ) electrolyte, and we summarize and analyze the electrochemical, redox characteristics of the cell and long-term operational stability are summarized and analyzed. Based on the symmetric structure of SOFCs, the cathode and anode possess the same electrode material and there is no isolation layer in direct contact between the electrode and electrolyte. This is not only an innovative attempt in the field of solid oxide cell structure, but also an in-depth exploration of the development of future energy technology.

2. Experimental

2.1. Material Synthesis

The electrode material $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ was prepared by the 'sol-gel' method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were weighed according to the stoichiometric ratio and added into the deionized water sequentially, and then the beaker was placed on a magnetic stirrer and stirred at a rotational speed of 400 r/min, and then stirred until homogeneous. Then, according to the ratio of all metal ions in the solution: citric acid: EDTA=1:1:1, citric acid and EDTA were added to the mixed solution and dissolved completely, at which time the solution was dark green. The pH was adjusted by slowly adding ammonia to the solution until $\text{pH}=7$. It was observed that the solution gradually changed from dark green to dark purple. The mixed solution was placed in a thermostatic water bath, the temperature was adjusted to 90°C , and a digital constant-speed powerful electric mixer was used to stir at 300 r/min until a purple-brown colloid was formed. The wet gel was transferred to an oven at 200°C for 12 h to evaporate the water in the colloid to form a dry gel, and the sample swelled to brown in the oven. The dry gel was removed and ground for 2 h to obtain the precursor powder. The ground powder was put into the

alcohol in equal proportions to ignite, burn part of the organic matter, and then continue to grind the combusted powder for 2 h. Finally, the powder was placed in a high-temperature furnace and calcined at 1000 °C for 6 h to obtain the electrode powder. The electrode materials are synthesized as shown in Figure 1

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) was synthesized using the above

dissolution gel in similar steps, the white wet gel was placed in a 200 °C blast drying oven for 12 h to form a black blocky dry gel, and after grinding for 30 min, white powder was formed by adding alcohol ignited according to the above ratios, and then calcined for 2 h through a muffle furnace at 1000 °C to obtain yellow powder.

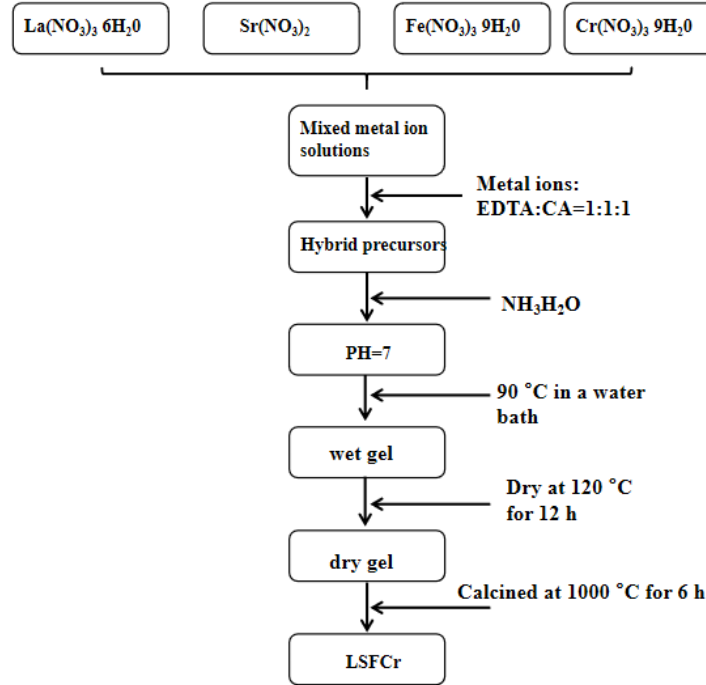


Fig 1. Flow chart of electrode material preparation

2.2. Cell preparation and Characterization

The electrolyte used was commercial powder Sc_2O_3 stabilized ZrO_2 (SSZ), and the SSZ powder was mixed and milled with PVA with a mass fraction of 5 wt% in a ratio of 4:1 by mass. During the milling process, the powder gradually changed from a viscous state to a filamentous state and finally to a loose powder state. An electronic balance was used to weigh 0.1 g into a mould with a diameter of 13 mm, and then a lever-type tablet press was used to fix the mould and apply a pressure of 4 Mpa, and the powder was kept for 1 min, which resulted in a flake-like powder. The flake-like SSZ was sintered at 1450 °C for 4 h to obtain the desired electrolyte flakes.

In order to further analyze the catalytic activity of the cell, the EIS and I - V - P performance of the cell will be tested in the range of 750-850 °C. The test environment will consist of cathodic measurements (air as oxidant) and wet H_2 (3% water) on the anodic side. Raw experimental data sets were analyzed using Zview 3.0 software). The relaxation time distribution (DRT) analysis framework pioneered by Ciucci's research group at the Hong Kong University of Science and Technology (HKUST) was used and the regularization parameter was set to 1×10^{-3} to solve the convolutional electrochemical impedance spectra.

3. Results and Discussion

3.1. Material Phase Analysis

Figure 2 shows the XRD pattern of calcination in air at 1000 °C for 6 h. The XRD pattern of LSFCr is shown in Figure 2. From the XRD pattern, it can be observed that shows a clear calcite structure, and the XRD pattern was analyzed by Jade software, and the characteristic peak of LSFCr was successfully identified. There are tiny stray peaks at 2θ values of 26-28°, and the stray peaks are analyzed as $\text{Sr}(\text{CrO}_4)$ by Jade, and the stray peaks do not affect the crystal structure of LSFCr. These peaks represent the positions of the reflected X-rays from different crystal planes and are labelled with the positions (2θ values) and relative intensities of the peaks. It is also possible to determine the spatial arrangement of the crystals by measuring the half-peak widths and intensities of the peaks, and by calculating the lattice constants and cell parameters. LSFCr powders were successfully synthesized by matching the diffraction peaks of the samples with the standard PDF (#97-016-7587) cards in the database of known crystal structures. LSFCr at 1000 °C is predominantly chalcocite structured with a space group of $R\bar{3}c$ (167) and a grain size of 228 Å.

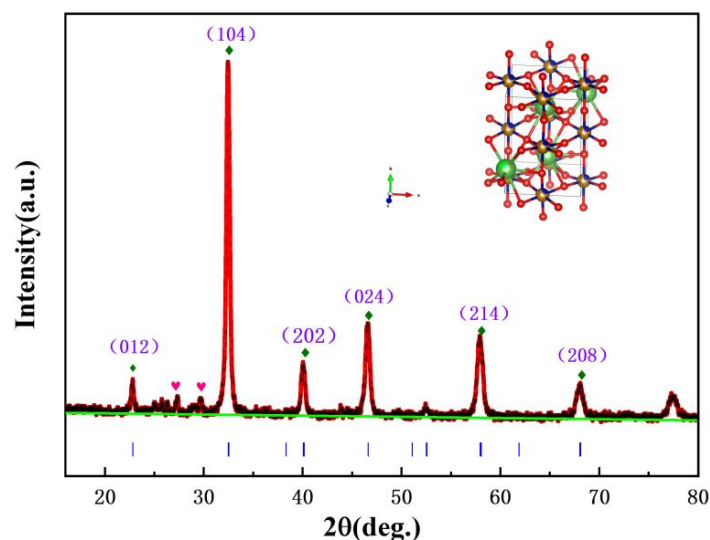


Fig 2. XRD spectrum of LSFCr sintered at 1000 °C for 6 h

3.2. Microstructural Characterization

The average size of the cross-section of LSFCr particles in Fig. 3(a) is about 500 nm, and the internal structure of the powder is loose, porous and relatively homogeneous, which is sufficient for the diffusion and transport of gases.

Figure 3(b) shows the cross-section microstructure of the symmetric cell, the thickness of the LSFCr electrode is about 40 μm, the picture shows that the LSFCr electrode and the

SDC, SSZ electrolyte are tightly bonded with the contact is very good, there is no delamination, which indicates that the LSFCr has a good adhesion, and this characteristic of the LSFCr provides a guarantee for the stable contact between the electrode and the electrolyte. The loose and porous electrode powder and dense electrolyte particles provide sufficient reaction interface for electrochemical reaction and reliable channel for ion transport.

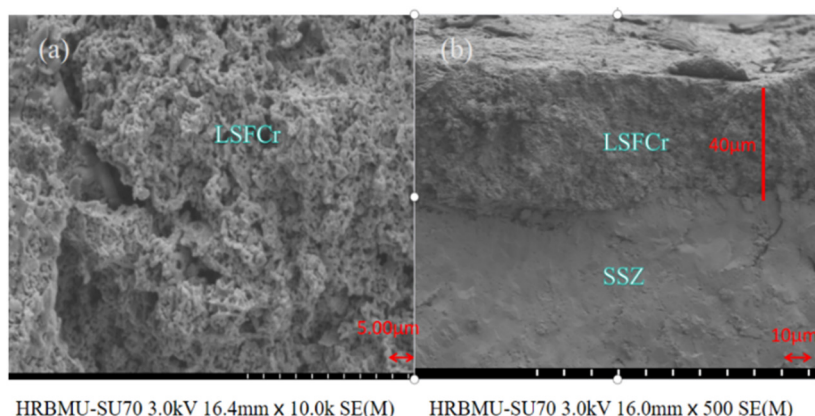


Fig 3. Scanning electron micrographs of LSFCr electrodes sintered at 900 °C for 2 h: (a) surface view of LSFCr electrode; (b) cross-section of LSFCr|SSZ|LSFCr

3.3. Electrochemical Properties and Cell Performances

The plots allow direct observation of the polarization resistance and the magnitude of the ohmic resistance, as well as the effect of temperature on the performance of the electrodes. As shown in Fig 4, the phenomenon that the ohmic resistance decreases as the test temperature increases can be observed. This indicates that the conductive properties of the electrode material are enhanced in a high temperature environment, thus reducing the ohmic resistance. In addition, it can be found that the polarization resistance value varies at different temperatures. At 750 °C, the polarization resistance is 1 Ω cm²; at 800 °C, it is 0.68 Ω cm²; and at 850 °C, it is 0.65 Ω cm². Compared with the polarization resistance at 750 °C, there is a decreasing trend in the magnitude of the resistance at 800 °C and 850 °C. The pattern of decreasing polarization resistance with increasing temperature is

obtained. The magnitude of the polarization resistance can reflect the strength of the electrocatalytic activity of the electrode materials. The electrocatalytic activity of the electrode material is enhanced with the decrease of the resistance value of the polarization resistance.

For the 800 °C data, a ZView fit was performed on the plots to obtain an equivalent circuit for the impedance spectrum as shown in Fig 4(b). In this circuit, L1 represents the inductance, R represents the ohmic resistance, (CPE1, R1) represents the high-frequency arcs, which are generated during charge transfer, (CPE2, R2), (CPE3, R3) represent the medium-frequency arcs, and (CPE4, R4) represents the low-frequency arcs, which represent the resistance generated during diffusion of oxygen ions on the surface of the cathode, oxygen dissociation and adsorption. The value of the polarization resistance (Rp) is equal to the intercept between the plot and the real axis, which describes the impedance resulting from the transfer of charge at the electrode-electrolyte interface

when an electrochemical reaction occurs. By comparing the fitted circuit with the original data, it was possible to find a good agreement between the experimental and fitted data,

which indicates that the equivalent circuit used provides a reasonable approximation.

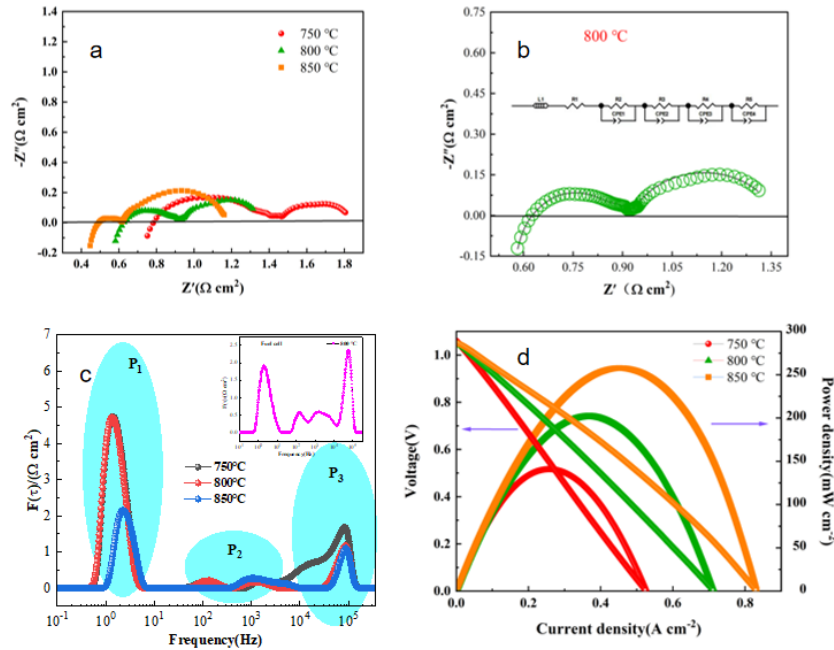


Fig 4. Electrochemical performance analysis of symmetric cell; (a) EIS; (b) fitted equivalent circuit diagram; (c) relaxation time distribution; (d) *I-V-P*

After testing, *I-V* curves and power curves in the range of 750 °C to 850 °C were obtained. At 750 °C, the open-circuit voltage is 1.06 V and the maximum power reaches 140 mW cm⁻². The maximum power increases to 201 mW cm⁻² as the temperature is increased to 800 °C, while at 850 °C, the

maximum power reaches 257 mW cm⁻². Comparison is made by different temperatures, and the open-circuit voltage decreases slightly and the power density increases gradually as the temperature is increased.

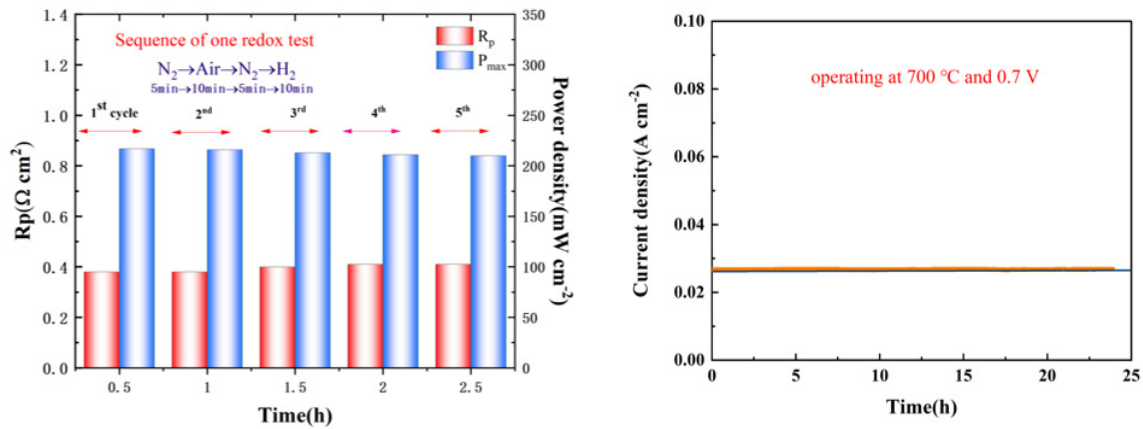


Fig 5. Symmetric cell stability and redox performance test

Five redox cycling tests were performed at 800 °C. The first step was to pass pure N₂ into the tube for 5 min to remove H₂. Each cycling process followed the following steps: in the first step, pure N₂ was passed into the tube for 5 min to exclude H₂; in the second step, N₂ was turned off and the system was left in an air atmosphere for 10 min to oxidize; in the third step, N₂ was passed into the tube again for 5 min to exclude the air inside the tube; in the fourth step, N₂ was turned off and pure H₂ was passed into the tube for the reduction, and after the atmosphere was stabilized, electrochemical tests were carried out, including impedance spectroscopy tests and maximum output power test.

As the cell underwent several redox cycles, the anode gradually reached a stable state, providing reliability for the long-term use of the cell. This also further confirms that the

LSFCr electrode material has good performance. The current density tends to be stable in 24 h, which shows that the LSFCr electrode material has good stability, and also proves that the battery with LSFCr as electrode material and SSZ electrolyte has excellent stability. This test result provides a strong support for the selection of battery electrode materials, and also lays a solid foundation for the application of the battery.

4. Conclusion

Successful preparation of LSFCr electrode materials by sol-gel method LSFCr sintered at 1000 °C for 6 h has good crystallinity. In the SEM test, the surface of the electrode is loose and porous, and the contact between the electrode and the electrolyte is very good without any separation

phenomenon. In the electrochemical test, as the temperature increases, the ohmic resistance and polarization resistance show a gradual decrease, reflecting the good conductivity and electrochemical reaction activity of the LSFcr electrode material; in the I - V - P curve obtained from the linear scanning test of the LSFcr electrode, the maximum power density of the cell at 800 °C can reach 201 mW cm⁻², with a higher power density; the LSFcr electrode has good crystallinity during the redox stability test reaction. In the redox stability test, the polarization resistance of the LSFcr electrode increases with the number of cycles and then tends to stabilize, and the maximum power density tends to stabilize; the current of the LSFcr|SDC|SSZ|SDC|LSFcr battery remains stable during the 24 h test period without any trend of degradation, which indicates that the battery has excellent stability for long-time operation.

References

- [1] Wang C, Xu Z, Koeppel B. A discrete element model simulation of structure and bonding at interfaces between cathode and cathode contact paste in solid oxide fuel cells. *Renewable Energy*. 2020; 157:998-1007.
- [2] Lu Y, Cai Y, Souamy L, Song X, Zhang L, Wang J. Solid oxide fuel cell technology for sustainable development in China: An over-view. *International Journal of Hydrogen Energy*. 2018; 43(28):12870-12891.
- [3] Mahato N, Banerjee A, Gupta A, Omar S, Balani K. Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science*. 2015; 72:141-337.
- [4] Zhang P, Huang Y H, Cheng J G, Mao Z Q, Goodenough J B. Sr₂CoMoO₆ anode for solid oxide fuel cell running on H₂ and CH₄ fuels. *Journal of Power Sources*. 2011; 196(4):1738-1743.
- [5] Zheng Y, Zhang C, Ran R, Cai R, Shao Z, Farrusseng D. A new symmetric solid-oxide fuel cell with La_{0.8}Sr_{0.2}Sc_{0.2}Mn_{0.8}O_{3-δ} perovskite oxide as both the anode and cathode[J]. *Acta Materialia*. 2009, 57(4): 1165-1175.
- [6] Zhang P, Guan G, Khaerudini DS, Hao X, Han M, Kasai Y, Sasagawa K, Abudula A. Properties of A-site nonstoichiometry (Pr_{0.4})_x Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-δ} (0.9 ≤ x ≤ 1.1) as symmetrical electrode material for solid oxide fuel cells[J]. *Journal of Power Sources*. 2014, 248: 163-171.
- [7] Ruiz-Morales J C, Canales-Vázquez J, Peña-Martínez J, López DM, Núñez P. On the simultaneous use of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} as both anode and cathode material with improved microstructure in solid oxide fuel cells[J]. *Electrochimica Acta*. 2006, 52(1): 278-284.
- [8] Wei T, Zhou X, Hu Q, Gao Q, Han D, Lv X, Wang S. A high power density solid oxide fuel cell based on nano-structured La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-δ} anode[J]. *Electrochimica Acta*. 2014, 148: 33-38.
- [9] Luo T, Liu X, Meng X, Wu H, Wang S, Zhan Z. In situ formation of LaNi_{0.6}Fe_{0.4}O_{3-δ}-carbon nanotube hybrids as anodes for direct-methane solid oxide fuel cells[J]. *Journal of Power Sources*. 2015, 299: 472-479
- [10] Liu X, Han D, Zhou Y, Meng X, Wu H, Li J, Zeng F, Zhan Z. Sc-substituted La_{0.6}Sr_{0.4}FeO_{3-δ} mixed conducting oxides as promising electrodes for symmetrical solid oxide fuel cells[J]. *Journal of Power Sources*. 2014, 246: 457-463.
- [11] Canales-Vázquez J, Ruiz-Morales JC, Marrero-López D, Peña-Martínez J, Núñez P, Gómez-Romero P. Fe-substituted (La,Sr)TiO₃ as potential electrodes for symmetrical fuel cells (SFCs)[J]. *Journal of Power Sources*. 2007, 171(2): 552-557.
- [12] Fan W, Sun Z, Bai Y, Wu K, Cheng Y. Highly stable and efficient perovskite ferrite electrode for symmetrical solid oxide fuel cells[J]. *ACS applied materials & interfaces*. 2019, 11(26): 23168-23179.