Characterization of (La,Sr)(Co,Fe)O$_{3-\delta}$ Ferrite-Based Cathodes for Intermediate-Temperature SOFCs

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Abstract

A-site deficient perovskite La$_{0.56}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (L56SCF) cathode for IT-SOFC application was prepared by solid state reaction. The mixture was calcined at 900-950°C for 3 h. The perovskite materials were re-ground, pressed into pellet shape and sintered at 1100-1150°C for 2 h. The preliminarily study of phase, microstructure, density and thermal expansion coefficient were characterized compared with the commercial La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$. It was found that L56SCF cathode sintered at 1100°C, 2 h showed single phase perovskite product with porous structure. The thermal expansion coefficient of the sample was 16.75×10^{-6} (°C)-1. It was found that L56SCF appears to be a candidate cathode for IT-SOFCs.

Key words: Ferrite-based cathode, LSCF, Perovskite, IT-SOFCs

Introduction

One of the main considerations of solid oxide fuel cells (SOFCs) is their high operating temperature (800-1000°C), leading to both physical and chemical degradation of construction materials. Moreover, this problem limits the choice of materials that can be used for SOFCs fabrication. Furthermore, this high operating temperature requires lanthanum chromite-based ceramic interconnectors to be used. These types of materials are very expensive. If the operating temperature could be reduced to 500-750°C, cheaper ferritic stainless steel (Fe-Cr alloy) could be replaced for the interconnectors. Such operating temperature enables to use not only cheaper interconnects, but also long-term stability materials and reduce the degradation of stack materials. Therefore it is necessary to lower the operating temperature of SOFC to an intermediate temperature range (500-750°C). However, this requires not only new cathode materials to be used, but also new development of cathode microstructure.

The traditional LSM cathode material is a poor ionic conductor at this intermediate operating temperature. A mixed electronic and ionic conductor, perovskite-type ABO$_3$ oxide, La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ system is one of the promising cathode materials for intermediate temperature-SOFCs (IT-SOFCs). Oxygen ionic conductivity is ascribed to the concentration of oxygen carrier (oxygen vacancy). The oxide ion conductivity can be improved by the creation of more oxygen vacancies.

The purpose of this study was to investigate the microstructure, phase and thermal expansion coefficient of prepared La$_{0.56}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (L56SCF) cathode. It has been anticipated that the sintering condition and particle size have the major influence on the performance of the prepared cathode.

Materials and Experimental Procedures

La$_{0.56}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (L56SCF) was prepared by the solid state reaction of La$_2$O$_3$ 99.99%, SrCO$_3$ 99.99%, Co$_3$O$_4$ and Fe$_2$O$_3$ 99%. The batch powders were ball milled for 24 h, dried and calcined at 900-950°C for 3 h, then re-milled for 24 h and sieved. These powders were dry pressed into pellets. The pellets were sintered in air in the temperature range 1100-1150°C. The perovskite phase was analyzed by X-ray diffractometer (JEOL JDX-3530). Scanning electron microscope (SEM, JSM-5410) was used for microstructure analysis. Density of the samples was determined by Archimedes method. The thermal expansion measurement was analyzed by using Anter Unitherm 1161 Dilatometer in the temperature range 30-700°C. Comparison of the samples prepared from L56SCF and commercial La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (commercial LSCF) provided from fuelcellmaterials.com (FCM) was investigated.
Results and Discussion

Physical Analysis

Table 1. Bulk density of L56SCF and commercial LSCF cathodes.

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial LSCF</td>
<td>L56SCF</td>
</tr>
<tr>
<td>1100°C, 2 h</td>
<td>4.42</td>
</tr>
<tr>
<td>1150°C, 2 h</td>
<td>5.51</td>
</tr>
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It was found that the average particle size of the prepared L56SCF powder of 0.37 μm was achieved and that of commercial LSCF powder was 0.64 μm. As shown in Table 1, the bulk density of L56SCF cathode sintered at 1100°C, 2 h is 5.02 g/cm³, which is lower than that of commercial LSCF sintered at 1150°C, 2 h (5.51 g/cm³).

Structural Study

An X-ray diffraction pattern for the calcined powders compared with the commercially available LSCF powder is shown in Figure 1. It was observed that calcination at lower temperature (900°C, 3 h) a cubic perovskite crystallized along with a second phase of strontium carbonate, as shown in Figure 1 (b). There was evidence of SrCO₃ at 2θ = 25°. At higher calcination temperature (950°C, 3 h), SrCO₃ decomposed, and the cubic perovskite converted to rhombohedral phase.⁷

![XRD spectra for LSCF powders](image)

Figure 1. XRD spectra for LSCF powders: (a) commercial LSCF; (b) L56SCF powder calcined at 900°C, 3 h and (c) L56SCF powder calcined at 950°C, 3 h.

Figure 2 shows the XRD spectra of each sintered composition (L56SCF and commercial LSCF cathodes). XRD analysis of the samples revealed the single perovskite phase product. All sintered samples confirmed full conversion to the rhombohedral perovskite system. The splitting of the peaks was found at 2θ = 40, 58 and 68°.⁷

Morphology of LSCF Samples

![SEM micrographs](image)

Figure 3. SEM micrographs of samples sintered at 1100°C for 2 h : (a) L56SCF and (b) commercial LSCF cathodes.
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2 h appeared to obtain lower porosity. Commercial LSCF hardly formed any sintering necks at 1100°C, 2 h. The appropriate sintering conditions for L56SCF and commercial LSCF were 1100°C, 2 h and 1150°C, 2 h respectively. It was in good agreement with the particle size where the larger particles (0.64 µm for commercial LSCF) required the higher sintering temperatures. The smaller grains (0.37 µm for L56SCF) with higher specific surface area are easier to be sintered and densified. Therefore, relatively low sintering temperature (1100°C, 2 h) was chosen for L56SCF to achieve the desired microstructure.

According to Figure 5, it was observed that the samples sintered at 1200°C, 2 h were over sintered. There was much less porosity comparing with the samples sintered at lower sintering temperatures. It was demonstrated that the microstructure of the sample appeared to be more densified. It has been expected that the structure of the cathode component has to be porous to allow oxygen ions diffusing through the electrolyte.

**Thermal Expansion Coefficient**

![Graph of Thermal Expansion Coefficient](image)

From Figures 3 and 4, it can be seen that the microstructure of L56SCF cathode sintered at 1100°C, 2 h was porous and in good contact to each other whereas the sample sintered at 1150°C,
As shown in Figure 6, the thermal expansion coefficient (TEC) of L56SCF and commercial LSCF cathodes were 14.55 and 14.92×10^{-6} (˚C)^{-1} (30-700˚C), respectively. It was report that the TEC of La_{0.6-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-δ} system reduced for z = 0.05, and slightly increased when z is increased. The recorded thermal expansion curves were linear, but they became steeper at high temperatures, as a result of the loss of lattice oxygen and the formation of oxygen vacancies.(2)

Next steps for this study are to investigate the electrical property and its correlation to phase, microstructure and TEC. More investigations will be reported at later stage.

Conclusions

La_{0.56}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3 (L56SCF) was prepared by the solid state reaction and compared with commercial LSCF cathodes. It shows that the samples exhibit single-phase rhombohedral perovskite structure. The microstructure of both L56SCF and commercial LSCF cathodes was similar while the average particle size of L56SCF cathode was smaller (0.37 µm) than that of commercial LSCF (0.64 µm) and achieved the lower appropriate sintering temperature (1100˚C, 2 h) with porous structure. In addition, at this sintering condition the bulk density of L56SCF (5.02 g/cm³) was lower than that of commercial LSCF (5.51 g/cm³) due to its higher porosity. With smaller particle size, the sintering temperature of the sample was lower.

It appears that L56SCF cathode can be a candidate for IT-SOFC cathode.

The TEC values in the temperature range 300-700˚C were 14.55×10^{-6} (˚C)^{-1} and 14.92×10^{-6}(˚C)^{-1} for L56SCF and commercial LSCF, respectively. These values are considered to be compatible with the TEC of CGO electrolyte [12.5×10^{-6} (˚C)^{-1}] (within ±20% range).(2)

Acknowledgements

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