

Crystal structure, thermal expansion and long-term behaviors of $\text{SmBaCoO}_{5+\delta}$ as cathode for intermediate-temperature solid oxide fuel cells

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Abstract. $\text{SmBaCo}_2\text{O}_{5+\delta}$ (SBC) was studied as cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The crystal structure, thermal expansion behavior, and electrochemical performance with long-term operation of SBC were characterized. An orthorhombic layered perovskite structure was observed in SBC cathode by a GSAS program for refinement. The average thermal expansion coefficient (TEC) is $21.6 \times 10^{-6} \text{K}^{-1}$ in the temperature range of 100°C - 800°C . For long-term testing, the polarization resistance of SBC cathode increases gradually from $25.77 \Omega \text{cm}^2$ for 2 h to $38.77 \Omega \text{cm}^2$ for 96 h at 600°C , and an increasing-rate for polarization resistance is around $13,8\% \text{h}^{-1}$. Based on the electrochemical properties, SBC cathode with mixed ionic and electronic conductor (MIEC) behavior is a potential cathode for intermediate temperature solid oxide fuel cells based on a SDC electrolyte.

1 Introduction

Fuel cell is an electrochemical device that converts chemical energy into electrical energy with high efficiency and low pollutant emissions [1, 2]. Intermediate-temperature (600 - 800°C) solid oxide fuel cells (IT-SOFCs) have been intensively investigated for both centralized and distributed power generations in the past decades [3-6]. Unfortunately, high performance and reliable for IT-SOFCs still remain a big challenge, mainly due to the sluggish oxygen surface kinetics at the electrolyte surface and reluctant oxygen reduction reaction (ORR) activity in the cathode [6].

The electrochemical activity of the cathode dramatically decreases with decreasing temperature. The cathode becomes the limiting factor in determining the overall single cell performance. Therefore, the development of new cathodes with high-electrocatalytic activity for the oxygen-reduction reaction is critical for intermediate-temperature solid oxide fuel cells (IT-SOFCs) [4, 5].

The commercialization of SOFC-technology has shown delayed progress due to the prohibitive cost per unit power and unverified long-term durability [4,7]. To achieve a guarantee of reliability, the examination of degradation mechanisms of SOFCs during long-term operation is necessary. Reactions between components are one of the main degradation mechanisms, and it' the cause of the fast degradation of SOFC performance because of resistive reaction-layers [8].

Co-based Perovskite oxides are promising cathodes, because they show higher oxide-ion conductivities at intermediate temperature (600 - 800°C). Numerous materials related to cobalt-based oxides have been reported such as $\text{PrBaCo}_2\text{O}_{5+\delta}$ [9], $\text{NdBaCo}_{2-x}\text{Ni}_x\text{O}_{5+\delta}$ [10], $\text{Ba}_{0,5}\text{Sr}_{0,5}\text{Co}_{0,8}\text{Fe}_{0,2}\text{O}_{3-\delta}$ [11], $\text{Sm}_x\text{Sr}_{1-x}\text{CoO}_{3-\delta}$ [12], $\text{GdBaCo}_2\text{O}_{5+\delta}$ [13], and so on.

In this paper, the double-perovskite structure oxide of $\text{SmBaCoO}_{5+\delta}$ (SBC) was prepared and characterized. The electrochemical properties with long-term testing of an SBC cathode on SDC electrolyte were analyzed over the intermediate temperature (600 - 800°C).

2 Experimental

2.1 Cathode and electrolyte materials preparation

$\text{SmBaCoO}_{5+\delta}$ (SBC) oxide was synthesized by the solid state reaction process as reported previously [14]. Stoichiometric amounts of Sm_2O_3 , BaCO_3 and CoO powders were used as starting materials. These powders were mixed under ethanol using zirconia balls for 12 h. The ball-milled mixture was dried and ground into a powder with mortar and pestle, and then calcined in air at 1100°C for 4 h.

The $\text{Ce}_{0,8}\text{Sm}_{0,2}\text{O}_{1,9}$ (SDC) powder was synthesized by co-precipitation using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Sm_2O_3 as the starting materials. These starting materials were dissolved in distilled water in stoichiometric ratio amounts and then added to an ammonia solution. The

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detailed preparation procedure of SDC is described in reference 14.

2.2 Material characterization

The structure of the sintered cathode powder was characterized by X-ray powder diffractometer (XRD; Rigaku D/MAX-2500V), with a scanning rate of 4°/min and scanning range of 20-80°, using a Cu K α (1.5418 Å) radiation source. The powder XRD pattern and lattice parameter was analyzed by Rietveld refinement using the GSAS program.

2.3 Thermal expansion coefficients (TECs) measurement

The pellet for determining the thermal expansion coefficient of the SBC was pressed into cylindrical form with diameter of 5 mm by uniaxial pressure. The SBC green body was sintered at 1200°C in air for 2 h. The thermal expansion coefficient (TEC) of the sample was investigated by a thermal mechanical analyzer (TMA) from room temperature to 800°C with heating rate of 10°C/min.

2.4 Symmetrical cell fabrication

Preparation of sample for symmetrical cell has been reported previously [14, 15], it can be described in detail as follows. The cathode paste consists of cathode powder, solvent, binder, and plasticizer. The cathode paste was applied by screen-printing on both sides of SDC electrolyte disk. On one side, the cathode paste was painted as the working electrode (WE) with surface area of 0.385 cm². The Ag reference electrode (RE) was placed away from the WE by about 0.3-0.4 cm. Such a distance was chosen to avoid measurement errors due to the misalignment of the working and counter electrodes [15-17]. The cathode counter electrode (CE) was placed on the other side of the SDC disk then heated at 800°C for 2 h in air.

2.5 Long-term testing of electrochemical property

The symmetrical cell measurement for long-term testing was carried out under air ($p(O_2) = 0.21$ atm) at temperatures of 600°C from 2 to 96 h at intervals of 4 h. The AC impedance measurement was performed using the VoltaLab PGZ301 potentiostat with frequency applied range from 100 kHz to 0.1 Hz with 10 mV AC signal amplitude. Under the cathodic polarized condition, the EIS was conducted as a function of the applied cathodic voltage (E). The EIS fitting analysis was performed with the Zview software. Linear sweep voltammetry was measured between -0.3 and 0.1 V with sweep rate 0.5 mV/s versus the RE.

3 Result and Discussion

3.1 SBC cathode characterization

Figure 1 shows the refinement of SBC patterns including the measured XRD data, the calculated profile and the difference between them. There are no peaks due to impurities in the structure of SBC, where the powder calcined at 1100°C, suggesting that the SBC is successful synthesis.

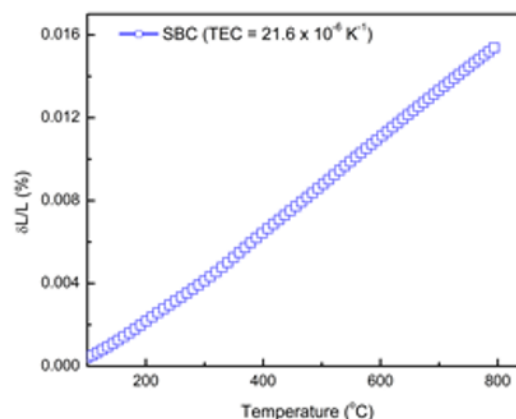


Fig.1. Observed (crosses) and calculated (solid line) XRD profiles and the difference (bottom line) for SBC cathode

Cell parameters regarding SBC obtained from the Rietveld refinement is listed in Table 1. The experimental data is highly agree with the calculated profiles, suggesting that cations are well ordered in the perovskite lattice [18,19].

Table 1. Crystallographic information for SBC measured at room temperature, cell parameters obtained by the Rietveld refinement*

Atom	Wyckoff position	x	y	z	Uiso	Occ.
SM1	2p (½ y ½)	1/2	0.23981	1/2	0.0174	1.0000
BA2	2o (½ y 0)	1/2	0.24946	0	0.0120	1.0000
CO3	2r (0 ½ z)	0	1/2	0.24619	0.0091	1.0000
CO4	2q (0 0 z)	0	0	0.24703	0.0058	1.0000
O5	1a (0 0 0)	0	0	0	0.0770	1.3871
O6	1e (0 ½ 0)	0	1/2	0	0.0021	0.8262
O7	1g (0 ½ ½)	0	1/2	1/2	0.2256	0.8367
O8	1c (0 0 ½)	0	0	1/2	0.0074	1.1426
O9	2s (½ 0 z)	1/2	0	0.19535	0.0753	1.1285
O10	2t (½ ½ z)	1/2	1/2	0.23585	0.1557	1.1552
O11	4u (0 y z)	0	0.25902	0.21623	0.0240	1.1849

*R_p = 0.20, R_{wp} = 0.23, R_{exp} = 0.23, orthorhombic (Space group:Pmmm), a = 3.8901 Å, b = 7.8099 Å, c = 7.5797 Å, v = 230.28 Å³

3.2 Thermal expansion coefficients of SBC

The thermal compatibility between cathode material and other components is the main factor related to the working stability of SOFCs. Since a large difference of the thermal expansion coefficients (TECs) between these components will introduce interfacial stress during thermal cycling and resulted in cracks and cell degradation [20]. The pellet used for determining the thermal expansion of SBC was sintered at 1200°C for 2 h in air. The TECs of the sample was measured by a thermomechanical analyzer from 1room temperature to 800°C and the result as shown in Figure 2. The average TEC of SBC is $21.6 \times 10^{-6} \text{ K}^{-1}$ and TECs at various temperature range are listed in Table 2. The SBC specimen shows a linear expansion in the low temperature region (100-300°C) and a slight increase in slope at higher temperatures region (300-800°C). At higher temperature, a part of the smaller Co^{4+} were reduced to larger Co^{3+} or Co^{2+} with a loss of oxygen, C^{3+} ions are easy to transit from low-spin to high-spin state [14,21-23].

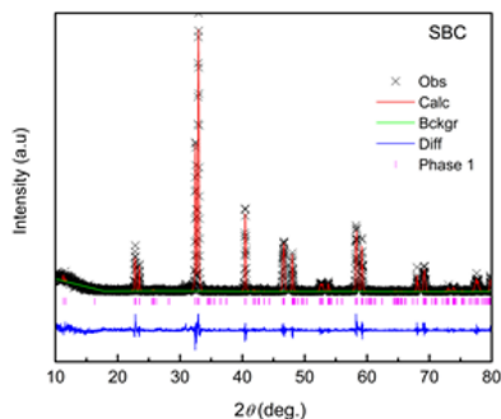


Fig.2. Thermal expansion behavior from 100°C to 800°C

Table 2. TECs for SBC at various temperature range

Sample	TEC x 10 ⁻⁶ (K ⁻¹)		
	100-800°C	100-300°C	300-800°C
SBC	21.6	18.8	22.8

3.3 Long term testing of SBC

To evaluate the stability the SBC for a long-time operation, the performance of a SBC|SDC|SBC symmetrical cell was tested, and polarization resistance (R_p) values were recorded dependence of time under stationary air at 600°C as shown in Figure 3.

The R_p values increased gradually with time from $25.77 \Omega \text{ cm}^2$ for the initial 2 h to $38.77 \Omega \text{ cm}^2$ for 96 h long-term testing. A slight increase in cathodic polarization resistance is observed that an increasing-rate is around $13.8\% \text{ h}^{-1}$ from the initial 2 h to 96 h. Cathode delamination from electrolyte may be one possible cause of increasing in polarization resistance at initial fast degradation [24]. The delamination between layers causes the decline of reaction site for ORR, leading to increase polarization resistance. The TEC

difference between SBC and SDC is approximately $5.3 \times 10^{-6} \text{ K}^{-1}$.

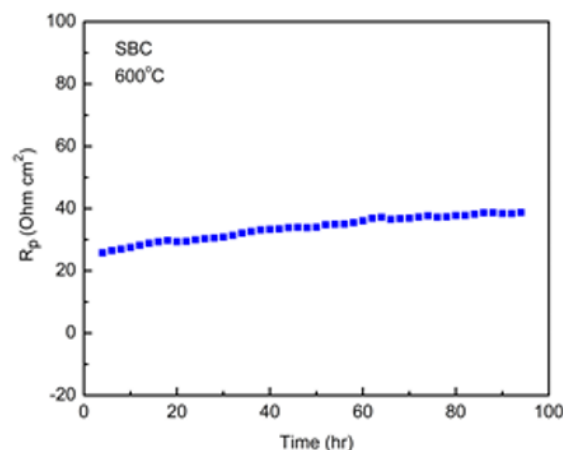


Fig. 3. Polarization resistance (R_p) of under static air at 600°C for long-term testing.

The interface may be easily detached during a 96h operation at 600°C due to the large TEC difference. With increasing the testing time, the following slow degradation in the MIEC-cathode performance may be several possible mechanisms such as (1) the grain size of SBC may coarsen [25], and (2) inter-diffusion may occur between SBC and SDC interface [26].

3.4 SEM images

The cathode microstructure is closely related to the electron and oxygen transportation, the reaction kinetics, charge transport, and mass transport preprocess. These properties influence the performance of solid oxide fuel cell [27,28].

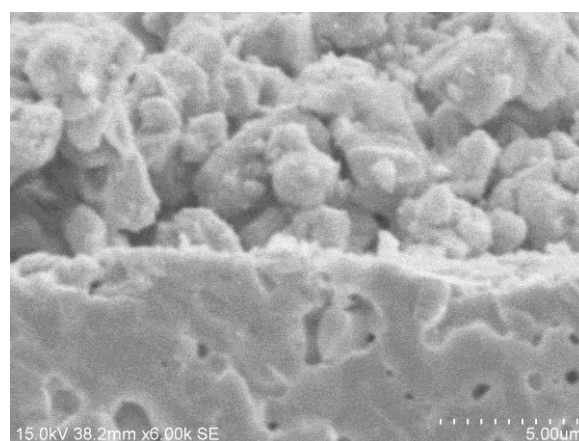


Fig.4. SEM image of cross-section view for SBC|SDC half-cell.

The microstructure of a cross-section of SBC|SDC half-cell as shown in Figure 4 revealed the adhesion between the cathode and electrolyte is quite good. The SBC particles distributed uniformly, and the particle size ranged from 1 to 2 μm .

4 Conclusions

This study mainly investigated the long-term performance of SmBaCo₂O_{5+δ} (SBC) as potential cathode material for IT-SOFC. For long-term testing, the polarization resistance of SBC increases gradually from 25.77 Ω cm² for 2 h to 38.77 Ω cm² for 96 h at 600°C and an increasing-rate for polarization resistance is around 13.8% h⁻¹. The average thermal expansion coefficient (TEC) value of SBC is 21.6 x 10⁻⁶ K⁻¹. At higher temperature, a part of the smaller Co⁴⁺ were reduced to larger Co³⁺ or Co²⁺ with a loss of oxygen, Co³⁺ ions are easy to transit from low-spin to high-spin state.

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