THERMAL EXPANSION BEHAVIOR
OF THE Ba_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3−δ} (BSCF) WITH Sm_{0.2}Ce_{0.8}O_{1.9}


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Submitted October 07, 2013; accepted March 5, 2014

Keywords: Nanomaterial perovskites, Cathode materials, Solid oxide fuel cell, BSCF, Thermal expansion coefficient

Nanostructured perovskite oxides of Ba_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3−δ} (BSCF) were synthesized through the co-precipitation method. The thermal decomposition, phase formation and thermal expansion behavior of BSCF were characterized by thermogravimetric analysis, X-ray diffraction (XRD), and dilatometry, respectively. XRD peaks were indexed to a cubic perovskite structure with a Pm3m (221) space group. All the combined oxides produced the desired perovskite-phase BSCF. The microstructures were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM analysis showed that BSCF powders had uniform nanoparticle sizes and high homogeneity. The cross-sectional SEM micrograph of BSCF exhibited a continuous and no delaminated layer from the electrolyte-supported cell. The thermal expansion coefficient (TEC) of BSCF was 16.2×10^{-6} K^{-1} at a temperature range of 600°C to 800°C. Additional experiments showed that the TEC of BSCF is comparable to that of Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) within the same temperature range. The results demonstrate that BSFC is a promising cathode material for intermediate-temperature solid-oxide fuel cells.

INTRODUCTION

Solid-oxide fuel cells (SOFCs) effectively convert chemical energy directly to electrical energy [1]. SOFCs can be improved through nanotechnology. The use of nanosized porous electrodes in SOFC can improve the conversion of chemical energy into electrical energy. Moreover, the processing temperature for SOFC material development can be decreased to an average level. Consequently, the material and fabrication cost will decrease, and the demand for the SOFC application will increase [2]. Shao et al. suggested the use of Ba_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3−δ} (BSCF) as a cathode material and of Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) as the electrolyte for intermediate-temperature SOFCs (IT-SOFCs) [3]. The Pm3m cubic perovskite structure of BSCF confers stability at operating temperatures of up to 800°C. BSCF is considered a suitable cathode material in SOFCs. The durable operational stability of SOFCs can be ensured by properly matching the thermal expansion coefficients (TECs) of the electrolyte and of the electrode layers. One distinguishing feature of cobalt-based cathode materials is their high TECs [4]. This specific characteristic is due to the electrostatic attraction inside the lattice, which causes atomic vibration and eventually leads to high thermal expansion. Most of the new studies reduce the TEC of BSCF by changing the BSCF composition and the synthesis method, as well as by reducing the operating temperature of SOFCs from a high temperature of approximately 1000°C to an intermediate temperature of 600°C to 800°C. The TEC of BSCF perovskites is closely related to the chemical expansion effects that result from changes in the point-defect concentration and spin state of cobalt ions [5]. Thus, a low TEC improves the electrode durability. A-site cation-deficient BSCF oxides are capable of such reduction, which makes them promising cathodes for IT-SOFCs. Thus, a low TEC can improve electrode durability [6].

In this study, Ba_{x}Sr_{1−x}Co_{y}Fe_{1−y}O_{3−δ} (x = 0.2 and y = 0.2) BSCF powders were synthesized by a co-precipitation method. The phase-evolution behavior and variations in the thermal expansion coefficient of the BSCF were investigated. A BSCF/SDC/BSCF symmetrical cell was fabricated to examine the adhesion between the two layers after thermal treatment. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were also conducted.
**EXPERIMENTAL**

$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), where $x = 0.2$ and $y = 0.2$, was synthesized by a co-precipitation method. $\text{Sr(NO}_3\text{)}_2$ (99 %, Sigma-Aldrich, Malaysia), $\text{Co(NO}_3\text{)}_2\times6\text{H}_2\text{O}$ (99 %, System, Malaysia), $\text{Ba(NO}_3\text{)}_2$ (99%, Merck, Germany), $\text{FeCl}_2\times4\text{H}_2\text{O}$ (98 %, Systerm, Malaysia), $\text{HCl}$ (37%, Merck, Germany), $(\text{NH}_4)_2\text{C}_2\text{O}_4\times\text{H}_2\text{O}$ (99 %, Merck, Germany), ethyl cellulose (Sigma-Aldrich, Malaysia), $\text{C}_{10}\text{H}_{18}\text{O}$ (90 %, Merck, Germany), and $\text{NH}_4\text{OH}$ (25 % $\text{NH}_3$ in $\text{H}_2\text{O}$, Merck, Germany) were used to synthesize a perovskite-oxide BSCF powder. The detailed procedure for BSCF synthesis was previously reported (Ahmadrezaei et al. 2013). All reagents were mixed, and the reaction was conducted at room temperature for 3 h. The mixture was then filtered by a vacuum-filtration system, and the collected precipitate was dried in an oven for 2 h at 110°C.

TGA (Jupiter 449F3, Germany) was subsequently conducted to determine the optimum conditions for calcination, which were determined as 900°C for 2 h. Thermal expansion analysis was then conducted on the cathode using a dilatometer (TEC, Netzsch DIL402C, Germany). The samples for TEC measurements were fabricated in cylindrical form using standard pressureless sintering (Ø: ~ 6 mm, h: ~ 10 mm). The analysis was performed in air at 30°C to 800°C. The powder crystal structure was analyzed via X-ray powder diffraction (XRD, Bruker D8 Advance, Germany) with CuKα radiation at an operating voltage and current of 60 kV and 60 mA, respectively. SEM results (Figure 1) show that the prepared BSCF powder consists of spherical and uniform nanosized particles. Commercial $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_x$ (SDC, 99 %, Sigma-Aldrich, Malaysia) was used as the electrolyte. An SDC electrolyte-supported BSCF cathode-film half-cell was fabricated and sintered at 500°C for 2 h. The detailed fabrication procedures for the BSCF cathode film and SDC electrolyte-supported cell were described in our previous study [7].

**RESULTS AND DISCUSSION**

Figure 2 shows the TG weight loss of the BSCF precipitate. The weight-loss percentage was calculated from the graph to explain the decomposition process. The measurements were conducted in air. An approximately 10.85 % weight loss was observed from 30°C to 200°C. This weight loss is attributed to the elimination of water and bound moisture in the BSCF. The 6.45 % and 22 % weight losses observed from 200°C to 220°C and from 300°C to 410°C account for the decomposition of barium nitrate and cobalt nitrate, respectively. The curve between 410 and 880°C in the TGA graph indicates a minor weight loss that can be attributed to iron nitrate decomposition. After a minor decrease in the strontium nitrate precursor content occurred at 880°C, the decomposition stopped at 900°C. At this temperature, the final oxide powder in the cubic perovskite phase was expected to appear. The generated BSCF powder was produced by sintering at 900°C, which allowed calcination at a low temperature to produce the BSCF cathode. This process is called chemical grinding because the decomposition of the precursor results in the formation of the desired perovskite phase.
The XRD patterns of the BSCF powder calcined at 900°C are shown in Figure 3. After calcination, a strong strontium iron oxide perovskite phase was observed. All the combined oxides produced the perovskite-phase BSCF. The observed peaks for the sample were indexed to a perovskite system with a Pm3m (221)-space group cubic perovskite (01-0756980) structure. The perovskite structure of the BSCF powder was reported in previous studies [7-9].

The TEM image of the BSCF powder is shown in Figure 4. The detailed morphology and structure of the calcined BSCF were determined by TEM, which analyzed individual particles. Compositional homogeneity and structural uniformity were observed for the BSCF powder. A small particle size allows sintering at low temperatures, induces optimal porosity for gas transfers, and lowers TEC [10-11]. Powders with reduced particle sizes improve the particle connectivity and triple-phase boundary density in fabricated SOFC electrodes. Consequently, the electrochemical activity of the electrodes can be optimized during SOFC operation. A uniform particle size distribution and compositional homogeneity were achieved by the co-precipitation method for particles with an average size of less than 50 nm.

The TECs of the electrolyte and electrode layers should match well to ensure the long-term operational stability of SOFCs. BSCF, which is considered a cobalt-based cathode material, has a high TEC. The TEC of BSCF is significantly higher than those of the mostly widely used electrolyte SDCs. The surface morphologies of the electrolyte and cathode after sintering were determined by SEM. Figure 6 shows a cross-sectional SEM image of the deposited BSCF-SDC pellet. The microstructure exhibits a continuous, fracture-free BSCF cathode film on the SDC substrate. No trace of BSCF cathode film detachment from the SDC substrate was observed in the cross-sectional image. In the BSCF samples, a large number of oxygen vacancies can form in the lattice at a low temperature. These vacancies shift the curving region to a lower temperature and thus positively affect the cathode performance. Cobalt-based perovskites generally possess high TECs (~ 20×10⁻⁶ K⁻¹). For example, the TEC of La₀.₃Sr₀.₇Co₀.₈Fe₀.₂O₃₋δ is approximately 21.0 ×10⁻⁶ K⁻¹ at a temperature range of 30°C to 1000°C [16-17]. Low TEC promotes long-term electrode stability. (BS)₁₋ₓCF oxides that are slightly deficient in (BS)₁₋ₓ-site cations are highly promising cathodes for...
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IT-SOFCs. These findings confirm that the TECs of BSCF are nearly identical to those of the most commonly used SDC electrolyte. The high thermal-expansion coefficient of BSCF can be reduced using (BS)$_{1−x}$-site deficient BSCF. This reduced coefficient improves the long-term stability of the cell.

CONCLUSIONS

A BSCF powder was prepared by the co-precipitation method. The advantages of the co-precipitation method over conventional chemical techniques include low processing temperatures (< 1000°C) and smaller particle sizes. The pure single-phase structure of cubic BSCF samples was confirmed by XRD. The thermal cubic structure confers a low thermal expansion coefficient, which is ideally suited for electrolytes such as SDC. The average TEC of BSCF is $16.2 \times 10^{-6} \text{ K}^{-1}$ at an operating temperature range of 600°C to 800°C. This value is comparable to those of commonly used electrolyte SDCs. In summary, BSCF is a promising cathode for IT-SOFC.

Acknowledgements

The authors would like to acknowledge Universiti Kebangsaan Malaysia and the Malaysian Government for research sponsorship under the Arus Perdana Grant project funding UKM-TK-AP-05–09 and UKM-AP-TK-08–2010.

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