Properties of BSCF-SDC Composite Cathode Powder for Low Temperature Solid Oxide Fuel Cell

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Abstract. Barium strontium cobalt ferrite (BSCF) demonstrates properties, such as ionic conductivity, superconductivity, ferroelectricity, and magnetic resistance. Thus, BSCF has been reported as an impressive and effective cathode material in terms of high conductivity, excellent oxygen transport, catalytic activity and a potential candidate for a low-temperature solid oxide fuel cell (LT-SOFC). In this study, the nanocomposite cathode BSCF–samarium-doped ceria (SDC) was developed for LT-SOFC, and the behavior of the nanoceramic powders was examined. The BSCF–SDC composite cathode powders were mixed through the high-energy ball-milling process at 550 rpm for 2 h. The powders were then calcined at 900 °C and 950 °C for 2 h. The composite cathode powders were characterized based on morphology and grain size by using field emission scanning electron microscope and ImageJ software. The element analysis, chemical bonding, and thermal properties of each sample were studied using X-ray diffraction and energy dispersive spectroscopy respectively. Based on the result obtain, secondary phase has triggered after through milling process and gradually increase when the calcination temperature has increase. It also found that the size of particles become easily agglomerated and bigger at increased of calcination temperature. For particles distribution all major element in composite cathode has uniformly and homogeneous. Results of this study confirm that selecting a suitable calcination temperature is important in eliminating secondary phases in the BSCF–SDC composite cathode and enhancing its properties.

1. Introduction

Fuel cell is a device that efficiently converts chemical energy to electricity in a silent and environmentally friendly way [1]. Among the various kinds of fuel cells, solid oxide fuel cells (SOFCs) as alternatives for energy conversion have shown certain advantages, including wide fuel flexibility, high energy efficiency, and exhaust heat [2]. SOFCs are one of the most important energy conversion devices with high oxygen vacancies [3]. Among the most promising oxides are those of the perovskite (ABO₃) type, which is a structure that combines considerable flexibility and chemical stability, thus
permitting custom tailoring of the material properties by doping the A or B sites with different elements and stoichiometries [4].

Among the various possible compositions, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$/barium strontium cobalt ferrite (BSCF) has emerged as one of the best aspirants for both applications, in particular, considering its high oxygen permeation and oxygen-ion diffusion [5]. Thus, the composition of BSCF was found to exhibit outstanding oxygen permeation fluxes. Under application of relevant temperature, BSCF is not stable when operated in atmospheres containing carbon dioxide due to the formation of carbonates, because of this fact the applicability of BSCF as a cathode for SOFC has been questioned. When BSCF membrane was being operated at temperature below 800°C, it will make oxygen permeation rate movement slower with time because of the phase transition. By this situation, cubic perovskite phase become not stable in air when below these temperatures [4].

BSCF is a cathode material that has been considered a favorable and highly potential candidate for low-temperature SOFC development in the last two decades. The use of high operating temperature (800 °C–1000 °C) will lead to many disadvantages that include chemical and mechanical instability and high cost during implementation. The conversion of high operating temperature to low operating temperature (400 °C–600 °C) is a possible solution for SOFC commercialization [6]. However, the structural instability of cubic BSCF phase at low temperature is a concern. Therefore, the investigations concerning the phase stability of BSCF and the corresponding properties are expected. In addition, variable in calcination temperatures were carried out to investigate the influence of it on the phase of BSCF-SDC composite cathode.

### 2. Materials and Method

BSCF–samarium-doped ceria (SDC) composite cathode powders consist of commercial BSCF (Kceracell, Korea) and SDC (Kceracell, Korea) composites that are mixed through high-energy ball-milling (HEBM) process (Fritsch Pulverisette 6, Germany). The composite cathode powders consist of 50 wt% BSCF and 50 wt% SDC powder. The mixing process was performed by using wet-milling method with ethanol as a mixing medium. This method was performed with speed of 550 rpm within 2 h at room temperature. The mixed powder was dried in an oven at a temperature of 80 °C for 12 h after the milling process. The dried mixed powder was placed in an agate mortar and pulverized. Then, the powder underwent calcination process using an electric furnace at a temperature of 900 °C and 950 °C for 2 h. Selection of calcination temperature are support by the literature, where 900 °C are set as a minimum temperature for BSCF phase recovery and elimination of the secondary phases [8]. Then, the calcined composite cathode powder was ground again using the agate mortar to produce fine powders. Table 1 summarizes the sample identification.

| Sample       | Milling speed/rpm | Calcination Temperature/°C |
|--------------|-------------------|---------------------------|
| BSCF         | -                 | -                         |
| BSCF 900     | -                 | 900                       |
| BSCF 950     | -                 | 950                       |
| BSCF–SDC     | 550               | -                         |
| BSCF–SDC 900 | 550               | 900                       |
| BSCF–SDC 950 | 550               | 950                       |

The composite cathode powder samples were characterized based on their phase identification and crystalline structure by using X-ray diffraction (XRD) (Bruker D8 Advance, Germany). The test was conducted at room temperature and metered by Cu Kα radiation, $\lambda = 0.15418$ Å. This diffraction pattern
was scanned in the range of 2θ, starting from 20° to 90°, with a step scanning of 0.02°. The analysis data were then defined using Eva Diffraction Plus software.

Element analysis was performed by using energy dispersive spectroscopy (EDS) through a scanning electron microscope (JEOL USA Scanning Electron Microscopes). EDS aims to obtain the area and spot elemental compositions. Images at low magnification in secondary electron imaging mode with an accelerating voltage of 15 kV can be collected. Prior to the process, the sample was in a conductive phase and then was coated with platinum through platinum plating for 60 s with a current of 20 A.

Morphology grain analysis was conducted by using field emission scanning electron microscopy (FESEM) (JSM 6700F-Jeol, Japan). FESEM was used to visualize extremely small topographic details on the surface or the entire or fractioned objects [7]. In this study, samples were made from ceramic materials and were coated with platinum because samples should be in a conductive phase to conduct electron radiation and read the desired image using FESEM. Then, ImageJ software (Version 4.18) was used to measure the average grain size of the sample.

3. Results and Discussion

Figure 1 illustrates the XRD diffractogram of BSCF and BSCF–SDC samples before and after through the calcination process with two temperatures. The XRD result for BSCF powder sample after being calcined at 900 °C and 950 °C denotes that the BSCF spectrum generates the same spectrum pattern with the pure commercial BSCF powder (JCPDS No: 55-0563). The powders exhibit an excellent purity with no secondary peak that is observed during the analysis.

The composite powder of the BSCF–SDC sample indicates that the secondary peaks of BaCO3 (JCPDS No: 71-2394) and Sr2FeO4 (JCPDS No: 42-0480) were observed in both milled powders. The formation of the secondary phase might occur because of the heating state, which was generated during the HEBM process. The formation of the secondary phase peak was clearly observed and generated many peaks when the composite powder was calcined at 950 °C. These phases were also known as surface carbonate that is formed from the reaction between alkaline-earth oxide (Ba and Sr) with CO2 during the calcination process. The formation of secondary phase should be eliminated because this phenomenon will affect the electrochemical performance of the sample. The sample that was calcined at 900 °C and 950 °C exhibits a BSCF peak at JCPDS No: 55-0563 and SDC peak at JCPDS No: 75-0157. This peak finding agreed with the result of the literature, where the minimum calcination temperature is at 900 °C for the BSCF phase recovery and elimination of the secondary phase [8].

![Figure 1. XRD diffractogram of the uncalcined BSCF, SDC, BSCF-SDC and calcined BSCF and BSCF–SDC powders at 900°C and 950°C temperatures.](image-url)
Figure 2 depicts the FESEM micrographs of the BSCF and BSCF–SDC samples that were calcined at 900 °C and 950 °C. The above-mentioned results denote that the particle becomes agglomerate as the calcination temperature increases. This phenomenon occurs because the particle size increases with the increase in calcination temperature, which then reduces the surface area. Different states of the particle size can be observed from the sample before and after through the calcination process. The calcination process strengthens the particle bond, but the small particle size will simplify agglomeration.

Figure 2. FESEM micrographs of BSCF and BSCF-SDC sample at different calcination temperatures.

Figure 3. EDS mapping of the BSCF calcined at 900 °C.
Figure 3 shows EDS mapping for BSCF powder that calcined at 900 °C. From the result, all element in BSCF which is barium, strontium, cobalt, ferrous have distributed uniformly at that temperature. This is also shows the same result for temperature 950 °C. The quantitative result shows that Sm has displays the higher atomic percent by 42.76 and follow by Sr, Co and Fe.

Figure 4 displays the EDS mapping of the BSCF–SDC calcined at 900 °C and 950 °C. The EDS spectrum reflects the intensity of the elements contained in the BSCF–SDC composite cathode powder. The results indicate that all major elements, such as barium, strontium, cobalt, ferrous, samarium, and ceria, have distributed uniformly and homogeneous. The result also shows that all elements for BSCF-SDC that related to the phases in XRD results has been observed through EDS analysis and it’s still exist after milling process at speed of 550rpm and calcination process at 900 °C and 950 °C. The quantitative result of EDS depicts the amount of each element in percentages of the atom. The BSCF–SDC calcined at 900 °C and 950 °C displays the highest atomic percentage for Sm, followed by Co, Fe, Ce, Ba, and Sr. From the analysis, it can say that all element is able to withstand their structure towards the milling and heat treatment process.

Figure 4. EDS mapping of the BSCF–SDC calcined at (a) 900 °C and (b) 950 °C.
4. Conclusion

The phase stability of the BSCF and BSCF–SDC cathode powders was observed based on the effect of calcination temperature. The XRD result of BSCF-SDC cathode powder has shown that the BSCF phase peak was observed at a temperature of 900 °C. Meanwhile, the secondary phase can be clearly identified at 950 °C of BSCF-SDC cathode powder. The increasing of calcination temperature has led to easy agglomeration for the particle which will limit the surface area of the sample. Based on the EDS result, all element related to the phases in XRD result has been observed trough EDS analysis and its prove that all element still exists and can withstand with the milling speed and calcination temperature. Meanwhile, additional strategic research, such as a method for preparing composite cathode powder and studies on the LT-SOFC itself, should be conducted to overcome and evaluate the stability of the BSCF and BSCF–SDC sample.

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