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Effect of Ag Addition on the Structural Properties of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ Composite Cathode Powder

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Abstract: Barium strontium cobalt ferrite (BSCF) materials are one of the effective cathode materials for solid-oxide fuel cells (SOFCs) because of their high conductivity and excellent catalytic activity for oxygen reduction and mobility. The ionic conductivity of this type of composite cathode can be improved by adding some catalyst materials to help enhance their electrode activity toward oxygen reduction reaction. This study aimed to investigate the effects of Argentum (Ag) as a catalyst material toward $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (BSCF-SDC) composite cathode powders. The powders were mixed by using high-energy ball milling (HEBM) at 550 rpm and went through calcination process at 950 °C. Then, the calcined BSCF-SDC composite cathode powder were dry milled with Ag at five different weight percentages, start with 1wt% until 5wt%. The powders were then characterized by various analytical methods. Firstly, X-ray diffraction (XRD) was used for phase and structure identification. Secondly, Zetasizer Nano ZS was used to determine particle size. Then, the Archimedes principle to examine density and porosity also Field-Emission Scanning Electron Microscopy (FESEM) to identify the morphology of each sample. XRD results demonstrated that there was existence of impurities on BSCF-SDC and BSCF-SDC-Ag composite cathode powder after went through calcination and mixing process. This situation occurs because of the reaction of alkaline oxide with CO_2 during the calcination process and can be triggered when the composite powder was mixed using HEBM method. Zetasizer results revealed that the powder particles size tends to increase with increasing amount of Ag addition and FESEM morphology also shows an enlargement on particle shape along with increasing of Ag amount. Furthermore, the porosity (20%-40%) and density show an acceptable value as a good property needed for SOFC cathodes. All these findings indicated the effectiveness Ag addition has shown positive results on the structural properties of BSCF-SDC composite cathode powder.

Keywords: *Silver; BSCF-SDC; SOFC*

1. Introduction

Fuel cell is an electrochemical energy conversion device that converts the chemicals hydrogen and oxygen into water and produces electricity during the process. The electrical power generated by fuel cell are created silently with an environmentally friendly way and efficiently zero pollution. Amongst all types of the fuel cell, Solid Oxide Fuel Cell (SOFC) has shown excellent and promising power generation technologies since it can convert the chemical energy in fuels form directly into electric power with high efficiency and low emissions [1]. It also operated with the clean conversion of chemical energy to electricity, low levels of noise pollution and can operate with different types of fuels [2]. Fabrication of SOFC system apparently demands rigid materials and crucial process that required high cost, and which made commercialization of SOFC difficult [3]. Thus, conducting SOFC at low temperature (400ºC-600ºC)

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is essential because through this transformation, economical metal alloys can be use, which will reduce the electrode sintering and drop of the interfacial diffusion between the materials [2].

Previous reports had discovered that perovskite structure material is a desirable and effective cathode material for SOFC. Most of the perovskites, for example, lanthanum, manganite, ferrites and cobaltite are considered as cathode materials that fulfil this criterion. The latest development of perovskites -structure material, Barium Strontium Cobalt Ferrite (BSCF) has impressive properties such as high conductivity, excellent catalytic activity for oxygen reduction and mobility, ionic conductivity, superconductivity, ferroelectricity, magnetic resistance and has verified that it is a decent material for the solid cathode [4]. Material combinations for the development of a new compound is purposely done to improve on cell performance as well as the other properties. A series of new cathode was fabricated by impregnating a mixed conducting phase (BSCF) with an ionic conducting phase (Samarium doped Ceria) which results in a significant improvement of the electrochemical properties. The ASR is greatly lowered by impregnating the ion conductive phase to the ion-electron mixed conductive phase. The result gathers that cathode polarization resistance is 0.546 Ωcm^2 at 600 °C for pure BSCF cathode, but 0.214 Ωcm^2 for BSCF–SDC. The SDC content has a great effect on the electrochemistry property of combined electrode [5]. The advantages of using doped ceria as material for SOFC include higher oxygen ion conductivity and lower interfacial losses with cathode and anode, increased stack lifetime and lower overall cost [6].

Another factor that contributes on enhancing the performance of the SOFC system is the catalyst material. This material can speed up the reactions between anode and cathode. Argentum (Ag) is a good catalyst material for oxygen surface adsorption and dissociation of molecular oxygen into atomic oxygen and oxygen surface diffusion, improving the overall oxygen surface exchange kinetics of BSCF electrodes [7]. Studies by previous researcher has shown that 1-5wt% of Ag addition as well as incorporation of LSCF-SDC composite cathode as a fine conductor which has improves chemical reaction. Moreover, an Intermediate Temperature -Solid Oxide Fuel Cell (IT-SOFC) with composite cathode Ag-BSCF material exhibited better performance as compared to a BSCF cathode by 48 % [8]. It has been a rising needs to develop cathode and electrolyte materials that are able to perform well in low temperature. Therefore, this study aimed to investigate the effect of Ag addition on the properties of BSCF-SDC composite cathode powder and the corresponding properties.

2. Materials and Method

BSCF-SDC composite cathode powder was mixing by milling commercial BSCF and SDC powder (Kceracell, Korea) through wet milling process. The ratio of BSCF:SDC is 50:50 in the composite powder. The milling process was conducted using High Energy Ball Milling (HEBM) and with ethanol as a mixing medium at 550rpm for the period of 2 hours. Ensuing the mixing, the powder was dried in the oven at 80 °C for 12 hours. Then, the calcination process was conducted to treat the composite powder using electric furnace at 950 °C. The calcined composite powder was crushed in an agate mortar to get the desired powder form and size. After that, treated BSCF-SDC composite cathode powder was placed again in a ball milling machine to underwent dry milling process by adding Argentum (Ag) with 1% - 5% of weight percentage. This dry milling process was performed at speed 150rpm within 30 minutes. The resultant BSCF-SDC-Ag was not calcined following the low speed milling as their crystalline phase still have considerable attainability. [9][10]. Table 1 tabulated the sample identification for further understanding.

Table 1 - Sample identification

Sample	Argentum addition (weight percentage, %)
BS-Ag0	0
BS-Ag1	1
BS-Ag2	2
BS-Ag3	3
BS-Ag4	4
BS-Ag5	5

3. Characterization Method

There are few tests that were involved in obtaining the desired result on the properties of BSCF-SDC by incorporation of Ag. X-ray Diffraction (XRD) (Bruker D8 Advance, Germany), is one of the analysis involved that is used to examine the phase and crystalline structure of the sample. XRD is commonly used for identification of unknown crystalline materials, minerals and inorganic compounds. This analysis was performed in room temperature using Cu Kα radiation, λ=0.15418 Å. The scanned diffraction pattern range are in between 20° to 90°, with 0.02° of step scanning. Then by using Eva Diffrac Plus Software, analysis of the data is obtained. Field Emission Scanning Electron Microscopy (FESEM) (JSM 6700F-Jeol, Japan) was performed to analyze the sample morphology and microstructure condition. To achieve the desired image of FESEM, the sample must be coated with gold as it is ceramic based. This step was carried out to ensure the sample is in the conductive phase and ready to be run with electron radiation and capture the image. Morphology of the sample structure can be observed by using FESEM. This result can be further strengthened by running the supported analysis of Nano-Particle Zeta-Sizer (Zetasizer Nano ZS, Malven, UK). The testing was performed to analyze the particle size of BSCF-SDC and BSCF-SDC-Ag composite cathode powders. This testing was conducted with powder suspension which was produced by mixing the mixed composite powder with deionized water. Then the mixture was stirred for 5 minutes using a Magnetic Stirrer Probe (Hanna Instrument, Italy). Effect of Ag addition on the BSCF-SDC composite powder can also be calculated using the Archimedes Principle to determine sample porosity and density. Before running the analysis, the sample must be shaped in pallet form of 13mm in diameter and ~1.0mm in thickness. The sample then underwent sintering process at 900 °C. Then, the pallet sample was soaked in distilled water for 24 hours. This step is done to ensure that all pore in the sample surface and body were filled with distilled water. Then, porosity and density of the sample were determined by using density kit (Mettler Toledo, United State) and the result was calculated using the following equation;

$$\text{Apparent Density} = \frac{W_d}{(W_w - W_s)} \quad (1)$$

$$\text{Percentage of Apparent Porosity} = \frac{(W_w - W_d)}{(W_w - W_s)} \times 100 \quad (2)$$

Where:
W_d = Dry sample weight
W_w = Wet sample weight
W_s = Soak sample weight

4. Experiment Result

The result of XRD analysis for BSCF-SDC and BSCF-SDC-Ag composite cathode powder was as illustrated in Figure 1. Based on data collected, it shows that intensity pattern of the basic material is generated at common spectrum and the existence of the phase structure of the material which observable at JCPDS no: 00-005-0563 (cubic crystal) for BSCF , JCPDS no: 01-075-0157 (faced-center cubic) for SDC and at JCPDS no: 01-004-0783 (faced-center cubic) for Ag. In the making of BSCF-SDC-Ag composite cathode powder, there a lot of phases that were involved in getting the output. No change in phase and crystallinity was observed on the main material in the sample even after all stages occurred. However, impurities are detected on XRD diffraction peaks. There is secondary peaks of Barium Carbonate ($BaCO_3$) (JCPDS number: 01-071-2394) and Iron Carbonate ($Fe(CO_3)$) (JCPDS number: 01-083-1764) observed in the graph. Based on Fig. 1, formation of the secondary peaks is likely to occur as it gets nearer to BSCF and SDC peaks. This is because of the reaction of alkaline oxide with CO_2 during the calcination process. Supported by previous study had say that there are several potentials this secondary phase or impurity ions existed in the BSCF system even after the calcination process [9][11]. Besides, this formation of impurities also might be appear when the composite powder was mixed using HEBM method that involve of high speed that triggered the particle to break because of the impact forces that occurred during the conversion of kinetic energy [11]. On the other hand, the occurrence of impurity from BSCF material has made the crystallite percentage turn to 28.83% while for SDC it is still stable at the original crystallite phase.

Besides that, after 1% - 5% of Ag was mixed into the BSCF-SDC composite cathode powder, two secondary peaks were observed, namely Barium Iron Oxide ($BaFe_2O_4$) and Ceria Oxide (CeO_2) with JCPDS number: 00-025-1191 and 00-043-1002 respectively. The crystallinity percentage for BSCF (40.65%) and SDC (59.93%) element having changers according to development of impurity is triggered by their element. This situation is related to the impurity ions that could still remain as separate phases when the sample was calcined at temperature 950 ºC [11]. Appearance of CeO_2 is also contributed by the crystallite size of the material. When the size is too big, a lot of excess heat was generated which led to the growth of crystallite and caused agglomeration [12]. Moreover, majority of these impurities were successfully incorporated into BSCF lattice. FESEM was performed to identify the morphology and microstructure of each sample. Fig. 2 displays the micrographs of FESEM images at 30Kx in magnification with scale 100nm. In this magnification, the particle shape can be clearly observed. The particle shape can be further confirmed by the Zeta Sizer ZS result. It can also be observed that increased amount of Ag has led to particle agglomeration as shown by the red circle. Agglomeration most probably caused by removal of remaining carbon dioxide during calcination process which in turn led to strong bonding within each elements [13].

The particle size of both BSCF-SDC and BSCF-SDC-Ag was compared through particle size analysis via Zetasizer ZS. Table 2 shows the average particle size of BSCF-SDC and BSCF-SDC-Ag. The result shows that the particle size tends to increase with increasing of Ag amount. These results were found to be in parallel with FESEM micrograph in which the particle shape increase as the amount of Ag increase.

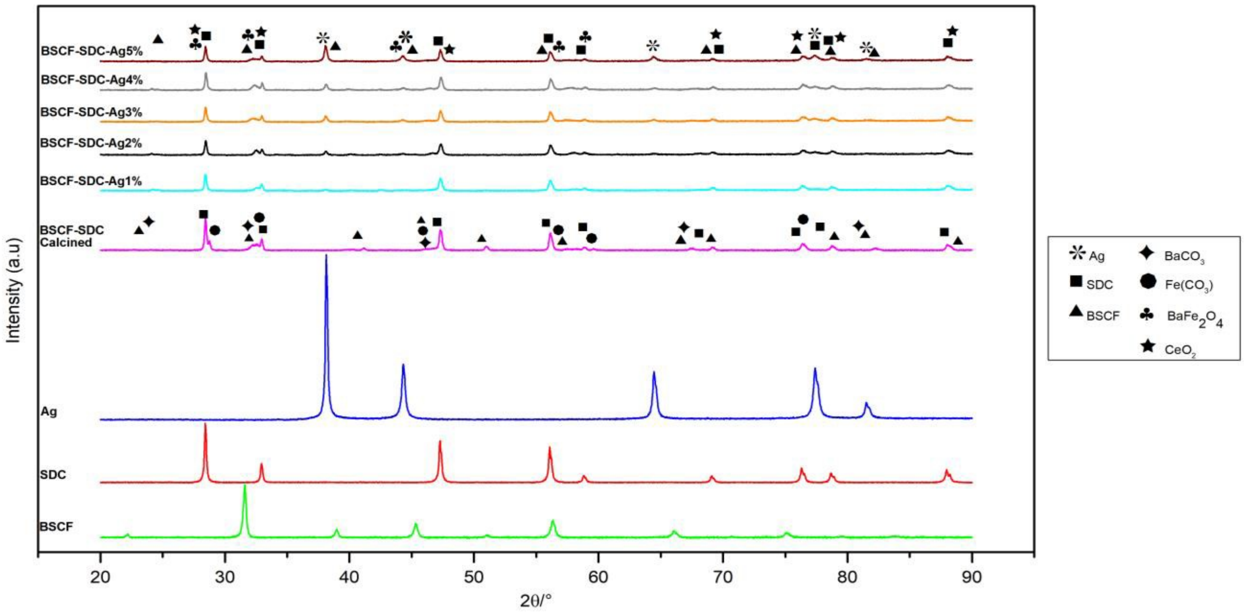

Fig. 1 - The XRD spectrum pattern for BSCF-SDC and BSCF-SDC-Ag composite cathode powder

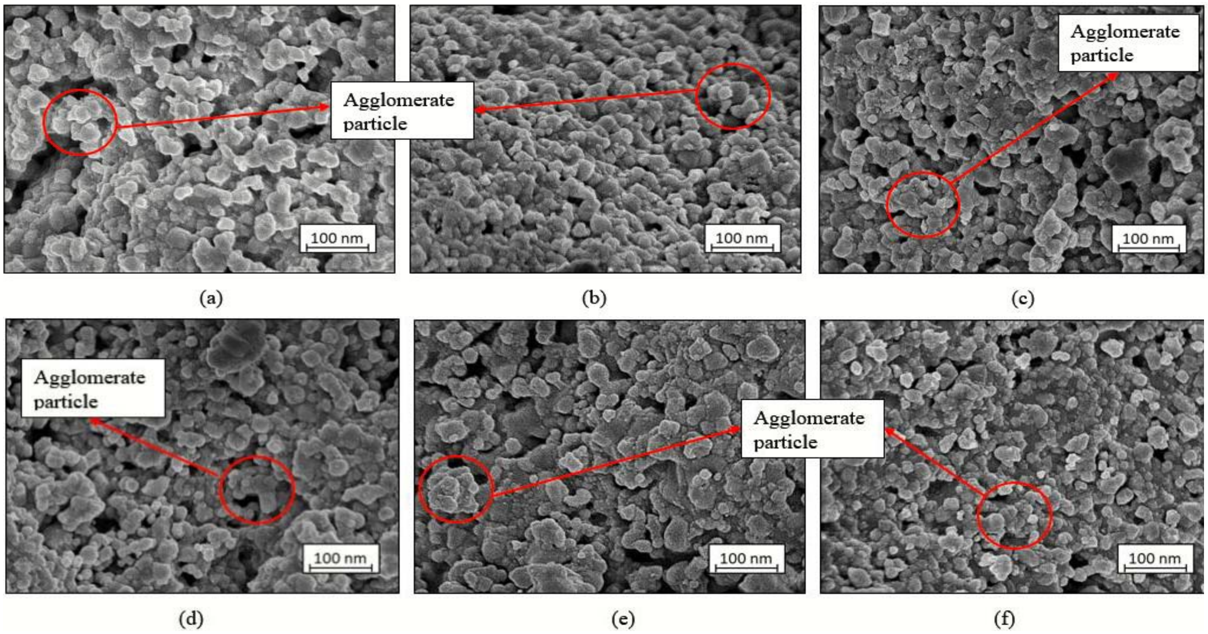

Fig. 2 - FESEM morphology of; (a) BS-Ag0; (b) BS-Ag1; (c) BS-Ag2; (d) BS-Ag3; (e) BS-Ag4; (f) BS-Ag5

Table 2 - Average of particle size for BSCF-SDC and BSCF-SDC-Ag composite cathode powder

Sample	Average particle size (nm)
BS-Ag0	351.6 ± 112.9
BS-Ag1	493.5 ± 71.14
BS-Ag2	712.3 ± 61.77
BS-Ag3	856.2 ± 43.84
BS-Ag4	987.2 ± 39.77
BS-Ag5	1181 ± 16.04

The Archimedes Principle was applied to investigate and calculate the properties of porosity and density of each sample. In addition, an acceptable porosity for a good SOFC sample is in the range of 20% - 40% [14]. Purpose to maintain the substrate at sufficient porosity for pellet sample is to allowed oxygen reduction reaction (ORR) to occur by permitted oxygen flow through the cathode-electrolyte region [15]. Table 3 tabulated the apparent percentage of porosity and density for BSCF-SDC composite cathode with different percentage of Ag. As shown in Fig. 3, the average porosity of the sample has the tendency to decrease while its density increased as the amount of Ag is also increased. The increasing amount of Ag has resulted to further agglomeration of the particle [16] as it is mixed with BSCF-SDC composite cathode powder. The increase in particle size leads to the decrease of sample porosity which in turn increase the sample density. Overall, the obtained porosity for all samples in this study has fulfilled the required porosity to be used as a cathode in SOFC which is in the range of 20% - 40% [14].

Table 3 - Average of porosity and density for different percent of Ag in BSCF-SDC composite cathode sample

Composition of Ag (wt.%)	Porosity	Density (g/cm^3)
0	36.45 ±	3.95 ±
1	36.34 ±	3.97 ±
2	36.04 ±	4.01 ±
3	35.40 ±	4.06 ±
4	35.36 ±	4.10 ±
5	35.34 ±	4.14 ±

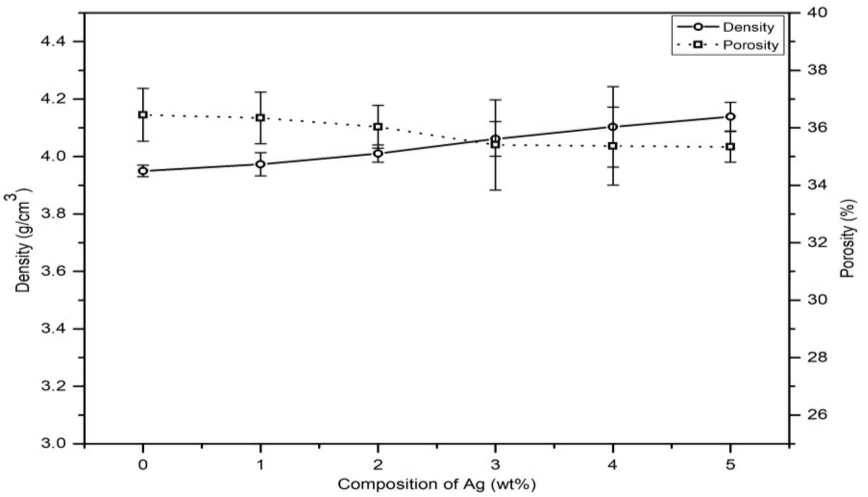

Fig. 3 - The apparent percentage of porosity and density of BSCF-SDC composite cathode with a different percent of Ag

5. Conclusions

The overall aim of this paper is to study and investigate the effect of Ag addition on the structural properties of BSCF-SDC composite cathode powder. As a summary, all result obtained has shown positive linkage respectively. Based on the XRD results, there are existence of secondary peaks [$BaCO_3$ and $Fe(CO_3)$] which took place when the composite powder was treated during calcination process. The existence of secondary peaks is due to the reaction between the alkaline earth oxide element (Ba and Sr) with CO_2 during the heat treatment process. Otherwise, other impurities were detected, namely $BaFe_2O_4$ and CeO_2 in the BSCF-SDC-Ag composite powder, which proven that the impurity ions could still remain as separate phases after it is dry milled with Ag material (1-5wt%). The morphology result also shows the increase in particle shape and sample has the tendency to agglomerate with the increasing amount of Ag addition. Data generated from Zeta-Sizer analysis has also reported that sample particle size increase along with increment of Ag amount. Finally, the result for porosity and density shown an acceptable requirement range for porosity which is in between 35.34% to 36.45% and density of about $3.95 g/cm^3$ to $4.14 g/cm^3$. Remarkably, the selection of material and parameter must be carefully done in a way to avoid any disturbing influences on the properties and stability of the composite cathode powder. Based on the previous literature and this research, Ag addition has shown positive results on the structural properties of BSCF-SDC composite cathode powder.

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