CHARACTERISATION AND AREA-SPECIFIC RESISTANCE ANALYSIS OF BARIUM STRONTIUM COBALT FERRITE - SAMARIUM DOPED CERIA CARBONATE - ARGENTUM FOR SOLID OXIDE FUEL CELLS

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Abstract. One of the most challenging aspects of fuel cell technology is searching for appropriate materials that can address and compensate for solid oxide fuel cell (SOFC) weaknesses. This study focuses on a barium strontium cobalt ferrite-samarium doped ceria carbonate-argentum (BSCF-SDCC-Ag). Some experimental work has been done to investigate the material's potential use in low-temperature SOFCs. The experimental variables include chemical, physical, and electrochemical characteristics. The phase identification of the composite cathode powder was analysed and showed that all element intensity peaks appear at their respective JCPDS numbers, with no secondary peaks occurring. The morphology and element distribution analysis illustrated micrograph images and the mapping of the material demonstrated that all elements are properly distributed and mixed. Based on the findings of the porosity and density tests, each sample contained the acceptable range value of porosity between 21.12 % and 22.50 %. The electrochemical performance was analysed at 400 °C, 500 °C and 600 °C. In comparison to BSCF-SDCC, BSCF-SDCC-Ag 1 wt% had a greater ASR value. The ASR value drops in the BSCF-SDCC-Ag 3 wt% sample while increasing in the BSCF-SDCC-Ag 5 wt% sample. Apparently, when the temperature is set to high, the ASR value is inconsistent. This might be due to the symmetrical cell sample condition, since its surface is cracked. Overall, the BSCF-SDCC-Ag 3 % contributes to a decrease in the ASR value at temperatures 400 °C and 500 °C, but at 600 °C has a slight increase in ASR value of approximately 10.4 %. Thus, further exploration of the production technique and preparation procedure is crucial to ensure the cathode reliability and performance for SOFC application.

Keywords: Ag, BSCF, cathode, impedance, SDCC

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Introduction

The daily amount of energy consumed is steadily growing in various countries. Consequently, the main energy sources such as coal, natural gas and oil will become scarcer to fulfil the demand needed by society [1]. Thus, an alternate energy source has emerged in recent times to address and mitigate the issue of losses in main energy sources. Hydrogen energy, commonly known as fuel cells, is one of the alternative energy sources that is currently being explored [2,3]. A fuel cell is an electrochemical device that can convert chemical energy into electrical energy. The solid oxide fuel cell (SOFC) is the most common and well-known form of fuel cell [4]. In addition, SOFC systems offer high efficiency in generating power from fuels. Their flexibility in fuels and great electric energy efficiency make a major contribution to the problem of environmental sustainability when fuelled with biofuels [2,3].

Generally, the SOFC system must operate at a high temperature of more than 600 °C to function properly [4]. Moreover, SOFCs have certain benefits because of their high operating temperature (400 °C - 1000 °C) as compared to other fuel cell types [5]. According to Kuterbekov et al. [5], high operating temperatures can lead to some problems with sealing, electrode morphology, chemical stability of cell components and accessory heat resistance. As a consequence of these issues, the cost of cells is increased, and their useful lifespan is shortened [5]. Thus, decreasing the operating temperature to approximately below 600 °C or intermediate temperatures around 600 °C–800 °C is a strategy to make them more realistic [6]. The lowering of operating temperature may reduce the cell's material costs, thereby making it more economical. In addition, these materials will offer a longer lifespan and less degradation [7].

However, the search for appropriate materials that can address and compensate for SOFC's weaknesses is one of the most challenging aspects of this technology. Recently, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) has received a lot of interest as a cathode material because of its electrochemical stability with SOFC [8]. As a result of its high oxygen permeability and excellent stability, BSCF has emerged as a potential material for SOFC application [9]. In SOFC systems, characteristics of the electrolyte influence the reaction path, open circuit voltage, stability, mechanical behaviour and operating temperature of the cell. Given that the electrolyte is exposed to both the anode and cathode sites, it should be chemically stable throughout a broad range of oxygen partial pressures [10]. As reported by Shi et al. [10], doped CeO_2 ($Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)) is an excellent electrolyte material that has substantially better oxygen ion conductivity, particularly at intermediate temperatures. Research by Tan et al. [11] showed that BSCF-SDCC has features in low-temperature SOFC that were quite encouraging for the future.

In addition, the catalyst material is another component that contributes to the improved performance of the SOFC system. This substance can hasten the reactions that take place between the anode and the cathode [12]. As reported by Mosialek et al. [13], Argentum (Ag) is an excellent catalyst for oxygen surface adsorption, dissociation of molecular oxygen into atomic oxygen and oxygen surface diffusion, hence enhancing the total oxygen surface exchange kinetics of BSCF electrodes. Generally, additional investigation into the manufacturing method and preparation process is required to guarantee the cathode's dependability and performance when it is used in a SOFC application.

Materials and Methods

Commercial powders of BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$), SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) (Kceracell, Korea), lithium carbonate (Li_2CO_3) and sodium carbonate (Na_2CO_3) (Sigma–Aldrich, USA) were used in the production of the BSCF-SDCC composite cathode powder. The BSCF and SDCC were combined in an equal part mixture by a 50:50 ratio. The SDCC was produced by combining the SDC with a mixture of Li and Na carbonate in the proportion of 80:20 by using the wet milling technique at 150 rpm. The calcination procedure for the BSCF–SDCC was carried out at 600 °C. Furthermore, the BSCF-SDCC-Ag composite cathode was created by using the dry milling process at 150 rpm by adding commercial powders of Argentum (Ag) (Alfa Aesar, USA). The composite cathode powder was mixed with various weight percentages of Ag as a catalyst material. These weight percentages ranged from 1 %, 3 % and 5 %. After the preparation, the powder was compacted into a pellet sample. Afterwards, the sample was sintered at 600 °C. The chemical, physical and electrochemical characteristics of BSCF-SDCC-Ag powder and pellets were investigated. Then, X-ray diffraction (XRD) (Bruker D8 Advance, Germany) was used to identify the composite powder phase using Cu Kα radiation ($\lambda = 0.15418$ Å) at an ambient temperature with the scanning of the diffraction patterns in the angle 2 θ between 20° and 90°, with a step size of 0.02°. EVA software was used to analyse the result gathered. The composite cathode powder's morphology was determined by scanning electron microscopy (SEM) (Hitachi Tabletop3030, Japan) and element distribution by energy dispersive spectrometry (EDS) (EDX Oxford Instruments). The porosity and density of the composite cathode pellet sample were examined using the Archimedes method (Density Kit AY220, Shimadzu, Japan). Finally, the electrochemical performance of the sample was investigated using electrochemical impedance spectroscopy (EIS) (Autolab AUT302 FRA) and analysis using Nova software.

Results and Discussion

The XRD testing is carried out to examine the x-ray pattern, phase stability and lattice structure of composite cathode powder. The chemical compatibility between the components in BSCF-SDCC-Ag composite cathode powder may be determined through a phase stability analysis. Figure 1 shows the XRD spectrum pattern for SDCC, BSCF-SDCC and BSCF-SDCC-Ag 1 wt%, 3 wt and 5 wt% composite cathode powder. The spectrum patterns element peaks are identified using the JCPDS number. Commercial powders of BSCF have a JCPDS number of 00-055-0563 with a lattice structure of cubic and space group Pm-3m (221). Furthermore, the SDC have a JCPDS number of 01-075-0158 and a face-centred cubic lattice structure with space group Fm-3m (225). Meanwhile, the Ag JCPDS number is 00-004-0783 and the lattice structure is face-centred cubic with space group Fm-3m (225).

In addition, carbonate, the mixture of lithium carbonate (Li_2CO_3) and sodium carbonate (Na_2CO_3), has a JCPDS number pattern of 00-022-1141 and 01-070-9248, respectively. The Li_2CO_3 and Na_2CO_3 have a based-centred monoclinic structure with space groups of C2/c (15) and C2/m (12), correspondingly. Referring to the XRD graph, all of the elements have been found at the JCPDS number that corresponds to them and have an excellent purity with no secondary peak that can be seen. Moreover, the peak intensity of the Ag element, visible at 38°, rises in tandem with the percentage of Ag in the sample.

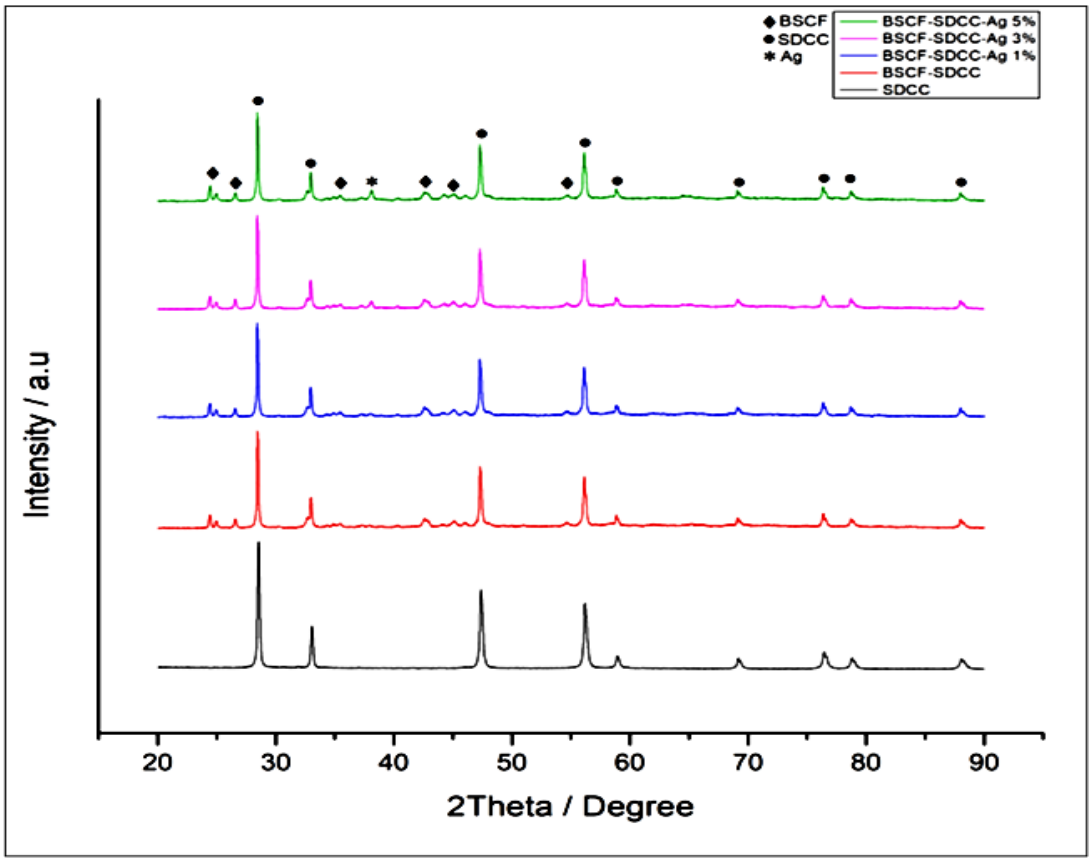


Figure 1: XRD spectrums pattern for SDCC, BSCF-SDCC and BSCF-SDCC-Ag 1 wt%, 3 wt% and 5 wt% composite cathode powder

The scanning electron microscopy (SEM) technique was used to discover the microstructure of the composite cathode powder. Figure 2, which presents the morphological picture of BSCF-SDCC and BSCF-SDCC-Ag (1 wt%, 3 wt% and 5 wt%), shows that agglomeration of the particle can be seen with an increasing amount of Ag addition [12]. Furthermore, agglomeration was most likely generated by the elimination of any remnant carbon dioxide during the calcination process, which in turn contributed to strong bonding within each element [14].

The energy dispersive spectroscopy (EDS) method was used to investigate the sample element distribution. Therefore, it is essential to initially achieve a homogenous state of powder that is distributed well across the sample area to create a good sample for SOFC. In this research, high-energy ball milling (HEBM) was used as a mixing medium to accomplish this condition. Figure 3 displays the EDS mapping and quantitative value of BSCF-SDCC-Ag 5 wt% composite cathode powder. Based on the figure, the sample was uniformly mixed during the milling process and it was distributed well. The quantitative table provides information on the atomic percentage of each element, and the mapping image is coloured in a variety of colours to depict the various types of elements.

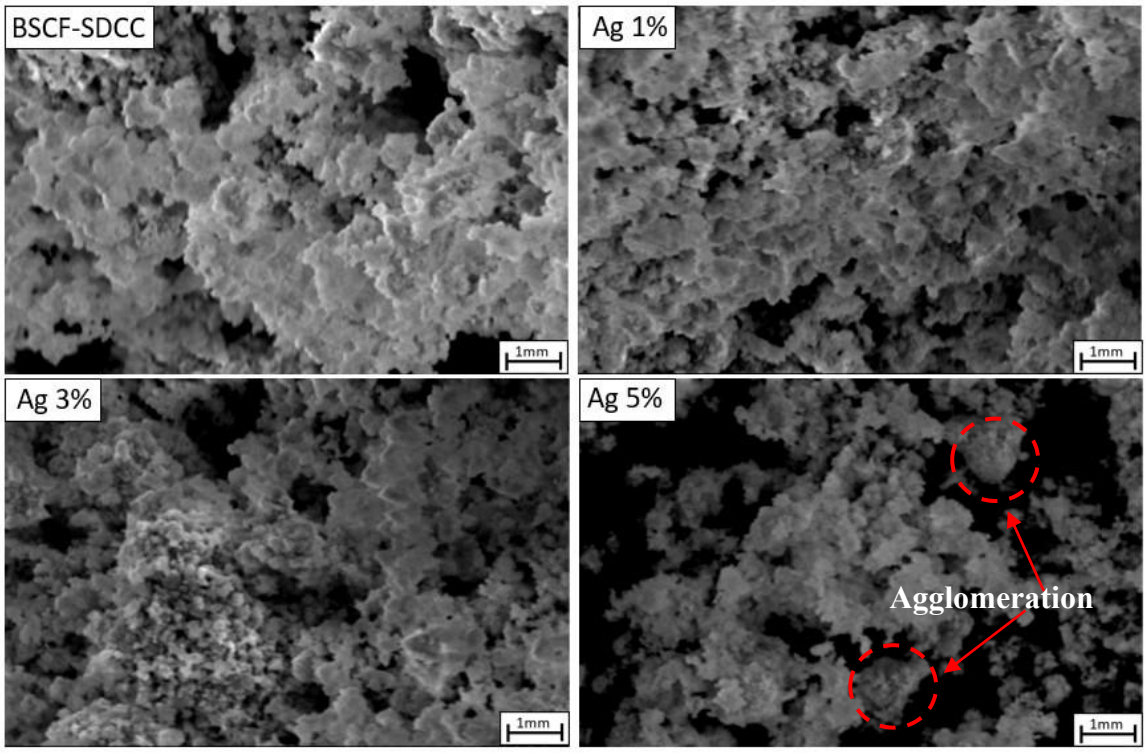
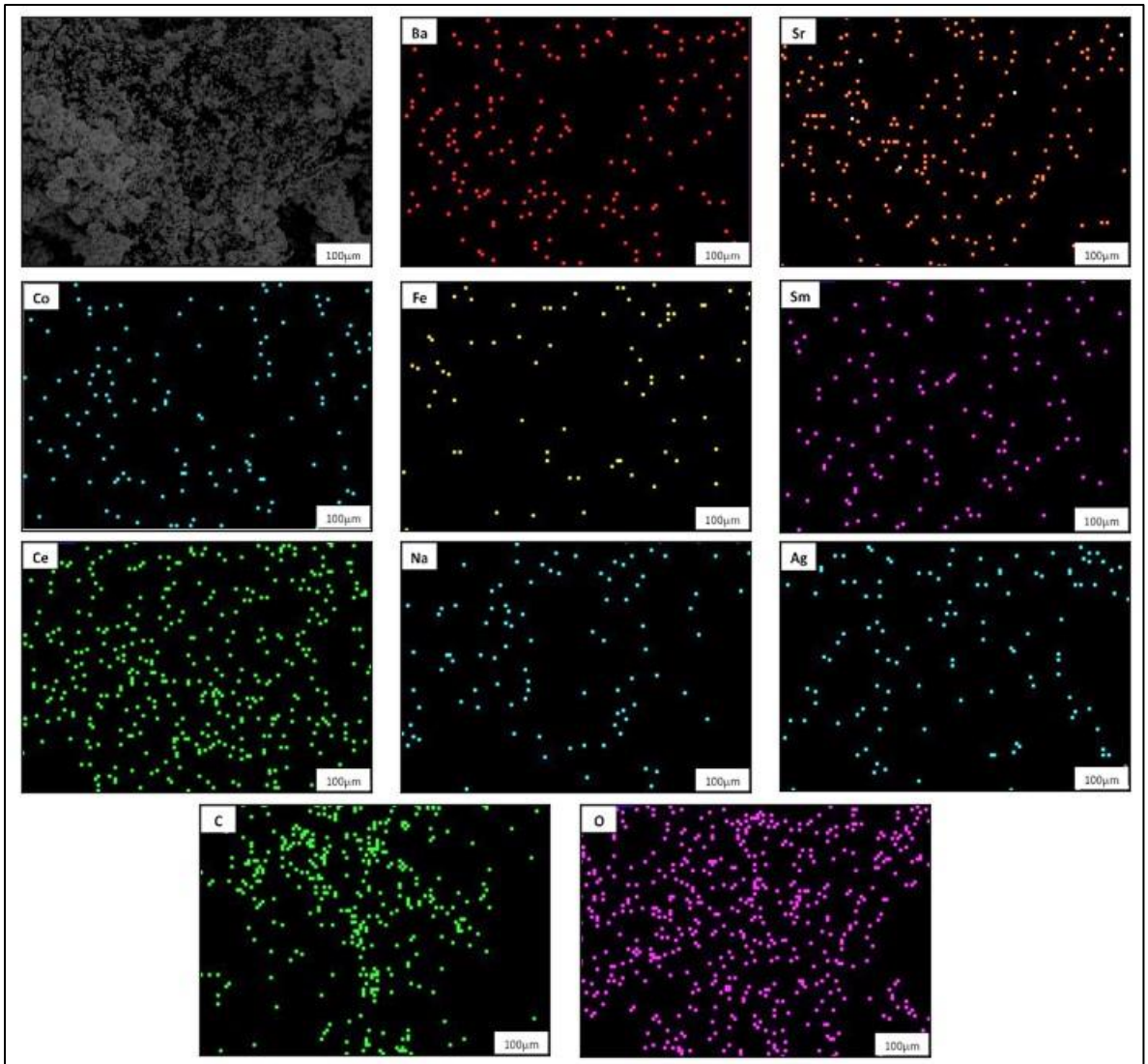


Figure 2: SEM morphology of BSCF-SDCC and BSCF-SDCC-Ag 1 wt%, 3 wt% and 5 wt%

The porosity and density of the sample were determined by applying the Archimedes Principle. A sufficient amount of porosity is one of the most important variables to consider while making a good composite cathode pellet sample. Porosity in the range of 20 %–40 % for the cathode cell is appropriate for a decent SOFC sample [15–16]. This porosity may be attained by sintering the material at a low temperature [16]. Table 1 shows the average porosity and density value for BSCF-SDCC and BSCF-SDCC-Ag (1 wt%, 3 wt% and 5 wt%) composite cathode pellets, meanwhile, Figure 4 illustrates the data for a clearer view. Based on the data collected, the porosity percentage of every BSCF-SDCC-Ag sample is much lower than the BSCF-SDCC by a difference of <3.2 %. Meanwhile, the density value of BSCF-SDCC-Ag has grown as compared to BSCF-SDCC by the contrast of <0.2 %. Thus, increasing the quantity of Ag addition causes the sample porosity to drop while increasing the density value, but the porosity value remains within the acceptable range of a good cathode cell [17].



Element	Atomic (%)
Ba	7.22
Sr	2.48
Co	6.75
Fe	0.52
Sm	8.32
Ce	21.26
Na	0.19
Ag	1.33
C	31.76
O	20.18

Figure 3: Element distribution and atomic percentage of BSCF-SDCC-Ag 5 wt% composite cathode powder

Table 1: The average porosity and density values for BSCF-SDCC and BSCF-SDCC-Ag (1 wt%, 3 wt% and 5 wt%) composite cathode pellets

Sample	Porosity (%)	Density (g/cm^3)
BSCF-SDCC	22.50 ± 1.88	3.63 ± 0.06
BSCF-SDCC-Ag 1%	21.12 ± 0.65	3.74 ± 0.03
BSCF-SDCC-Ag 3%	21.69 ± 0.41	3.76 ± 0.01
BSCF-SDCC-Ag 5%	21.78 ± 0.60	3.77 ± 0.01

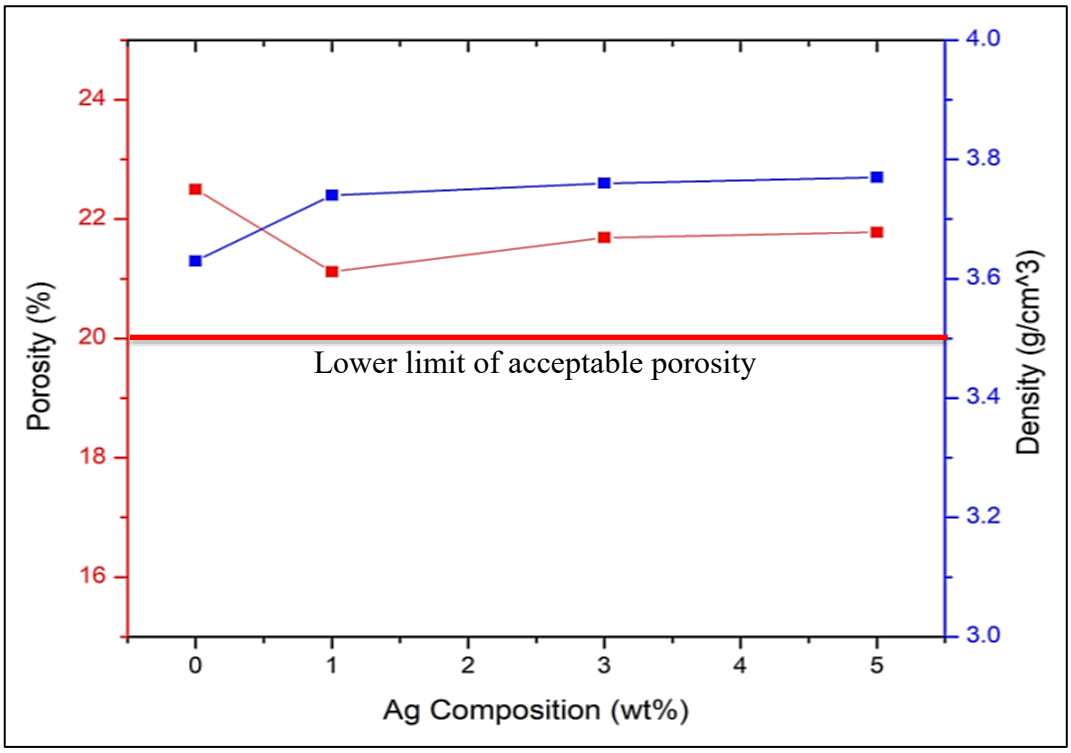


Figure 4: Porosity and density of BSCF-SDCC and BSCF-SDCC-Ag 1 wt%, 3 wt% and 5 wt% composite cathode powder

The impedance test was carried out to identify the electrochemical performance of BSCF-SDCC and BSCF-SDCC-Ag (1 wt%, 3 wt% and 5 wt%) symmetrical cell samples. Table 2 displays the area-specific resistance (ASR) value of the symmetrical cell samples at different operating temperatures. Based on the data recorded, it was shown that at 400 °C, the addition of 1 wt% and 3 wt% Ag reduces the ASR value whereas, at the 5 wt% of Ag addition, the ASR value rises. However, the ASR result is inconsistent when the temperature is set at 500 °C. This might be because of the symmetrical cell sample condition, as it cracks on the surface. The ASR value of BSCF-SDCC-Ag 1 wt% was higher than that of BSCF-SDCC. With the BSCF-SDCC-Ag 3 wt% sample, the ASR value decreases, meanwhile, in the BSCF-SDCC-Ag 5 wt% sample, the ASR increases. Similar to the ASR value at 500 °C, at 600 °C, the data exhibits that the ASR value for the BSCF-SDCC-Ag 1 wt% is greater as compared to BSCF-SDCC. The ASR value is lower for BSCF-SDCC-Ag 3 wt% as compared to BSCF-SDCC-Ag 5 % and thus significantly greater than that of BSCF-SDCC-Ag 3 %.

This indicates that adding 3 wt% of Ag assists to minimise the ASR value at 400 °C and 500 °C. However, the ASR value at 600 °C shows that the addition of Ag didn't show enhancement to help reduce the ASR value of the sample.

Table 2 shows the previous ASR value of the BSCF-SDC and BSCF-SDC-Ag (1 wt%, 3 wt% and 5 wt%) from Yusop et al. [17]. The data shows a decrease in the ASR value of each composite cathodes sample when the temperature increased. The ASR values for BSCF-SDC-Ag are ranging from 0.003 Ωcm^2 at 600 °C to 0.019 Ωcm^2 at 400 °C were much lower than BSCF-SDCC-Ag in this study. Besides that, the ASR values for SDCC based electrolyte studied by Rahman et al. [18] reported that the LSCF-SDCC has lower ASR value with a minimum of 0.69 Ωcm^2 at 600 °C and a maximum value of 266.6 Ωcm^2 at 400 °C. Figures 5 to 7 show the illustration graphs of comparison data between the previous study by Yusop et al. [17] with the collected experimental data.

Table 2: Area-specific resistance value of the symmetrical cell samples at different operating temperatures

Temperature (°C)	**Samples**	**Area Specific Resistance ASR (Ωcm^2)**	**Samples**	**Area Specific Resistance ASR (Ωcm^2) Yusop et al. (2020)**
400	BSCF-SDCC	70.33	BSCF-SDC	0.256
	BSCF-SDCC-Ag 1%	61.60	BSCF-SDC-Ag 1%	0.019
	BSCF-SDCC-Ag 3%	24.85	BSCF-SDC-Ag 3%	0.235
	BSCF-SDCC-Ag 5%	55.31	BSCF-SDC-Ag 5%	0.355
500	BSCF-SDCC	8.76	BSCF-SDC	0.023
	BSCF-SDCC-Ag 1%	21.03	BSCF-SDC-Ag 1%	0.012
	BSCF-SDCC-Ag 3%	6.55	BSCF-SDC-Ag 3%	0.023
	BSCF-SDCC-Ag 5%	8.88	BSCF-SDC-Ag 5%	0.128
600	BSCF-SDCC	1.73	BSCF-SDC	0.003
	BSCF-SDCC-Ag 1%	6.99	BSCF-SDC-Ag 1%	0.003
	BSCF-SDCC-Ag 3%	1.91	BSCF-SDC-Ag 3%	0.004
	BSCF-SDCC-Ag 5%	3.20	BSCF-SDC-Ag 5%	0.010

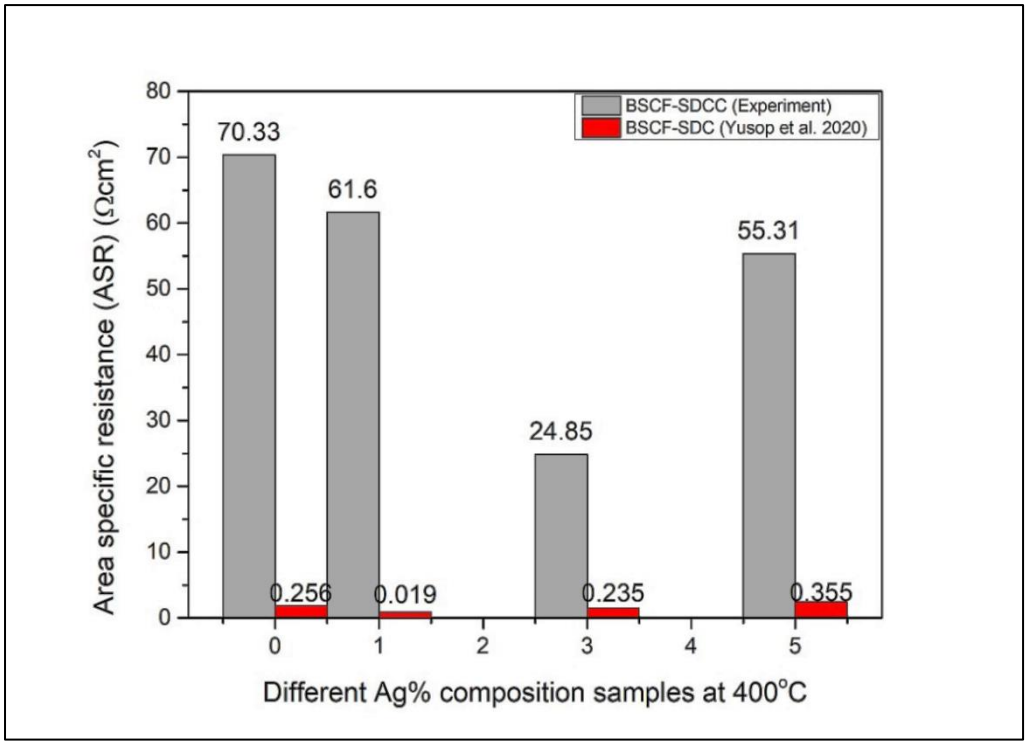


Figure 5: The comparison data of ASR value from the experiment with previous research at an operating temperature of 400 °C

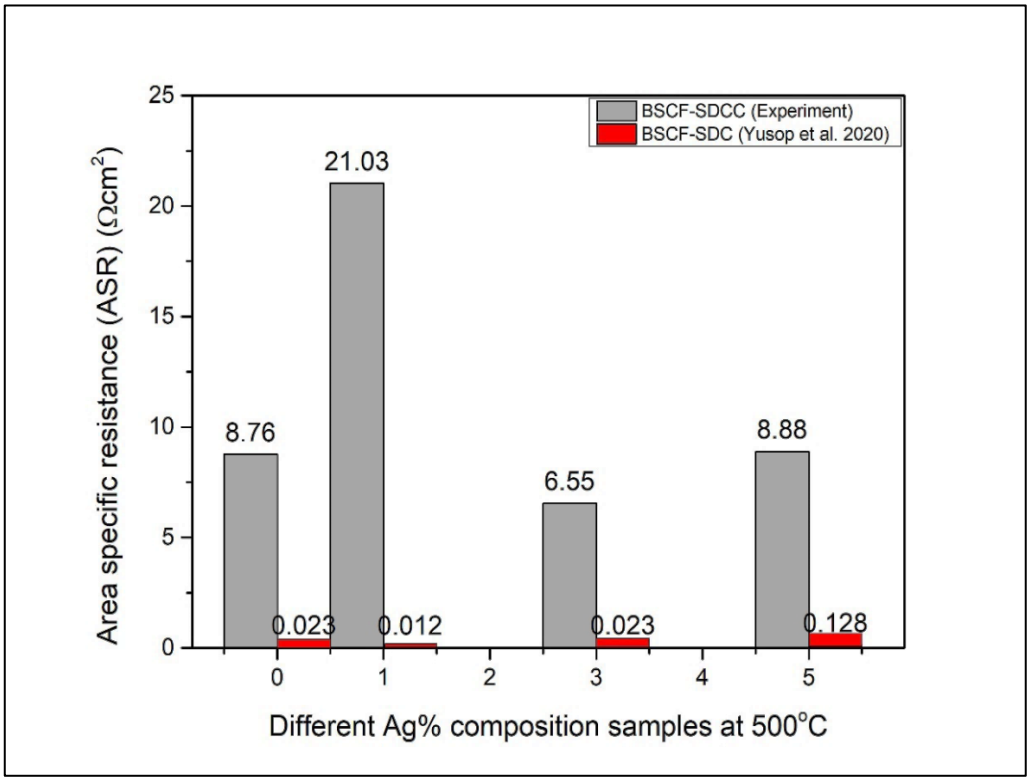


Figure 6: The comparison data of ASR value from the experiment with previous research at an operating temperature of 500 °C

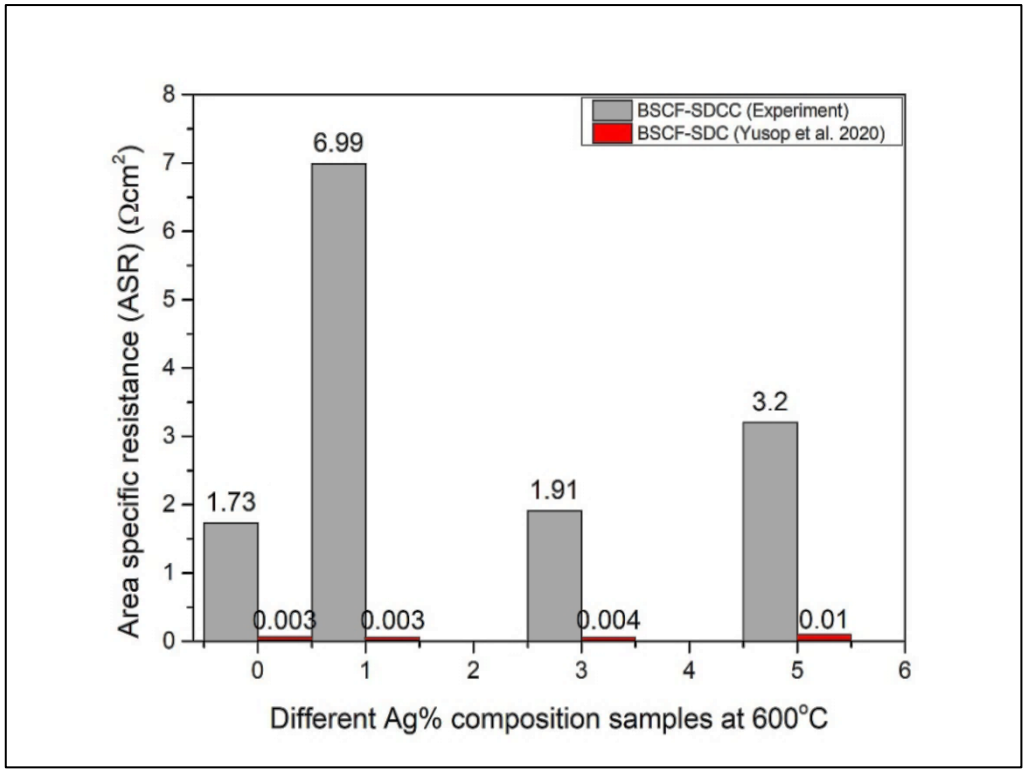


Figure 7: The comparison data of ASR value from the experiment with previous research at an operating temperature of 600 °C

Conclusions

In this study, BSCF-SDCC and BSCF-SDCC-Ag (1 wt%, 3 wt% and 5 wt%) composite cathode powder was made through a dry milling process using high-energy ball milling (HEBM). All of the samples were examined based on their chemical, physical and electrochemical properties. Based on the XRD pattern of the BSCF-SDCC-Ag, the peak intensity increases as the amount of Ag added to the samples increases. The porosity of BSCF-SDCC and BSCF-SDCC-Ag are in the range of 20 %–40 % which is acceptable for SOFC cathode. BSCF-SDCC-Ag sample has a porosity of approximately 21 %–22 % while a density of about 34 %–37 %. The higher percentage of porosity for BSCF-SDCC-Ag was reflected by the SEM images. The EDS mapping for BSCF-SDCC and BSCF-SDCC-Ag shows that all the elements in the composite cathodes are well distributed. The determination of the ASR value for BSCF-SDCC and BSCF-SDCC-Ag composite cathodes is slightly difficult because of the symmetrical cell sample surface defects in the form of cracks which appeared after going through the EIS testing at the temperature of 400 °C, 500 °C and 600 °C. Therefore, further exploration into the production technique and preparation procedure is crucial to ensure the cathode reliability and performance for SOFC application.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

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