Research Article

Electrochemical Properties of $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ Cathode Materials for Low Intermediate Temperature Solid Oxide Fuel Cells (LIT-SOFCs) Synthesized by Sol-Gel Method

Beyene Tesfaw Ayalew¹ and P. Vijay Bhaskar Rao²

¹Department of Physics, Wachamo University, P.O. Box 667, Hossana, Ethiopia

²Department of Physics, Wollega University, P.O. Box 395, Nekemte, Ethiopia

Correspondence should be addressed to Beyene Tesfaw Ayalew; beyenetesfaw@wcu.edu.et

Received 7 October 2020; Revised 27 December 2020; Accepted 26 May 2021; Published 29 June 2021

Academic Editor: Amelia Almeida

Copyright © 2021 Beyene Tesfaw Ayalew and P. Vijay Bhaskar Rao. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

$\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ (CSCFZ) powders were synthesized by the sol-gel method and characterized to study structural and electrochemical properties. X-ray diffractometer (XRD) patterns of all samples give nanosized particles of a high-degree crystalline cathode having a cubic-type perovskite structure of space group Pm-3m with the existence of oxygen vacancies in the lattices. The results have the perovskite phase with average crystallite sizes of 26.57 nm, 18.14 nm, 18.13 nm, and 18.12 nm with porosities of 9.93%, 9.87%, 9.50%, and 9.08% for $x = 0, 0.1, 0.15$, and 0.2 , respectively. Scanning electron microscope (SEM) micrographs showed the presence of pores on the microstructure. Average grain sizes of prepared samples found from SEM images were in the range of 105.30–183.02 nm. The partial substitution of zirconium at the B-site shows more stable materials than the host without decreasing the porosity that much. The results of electronic conductivity analyzed by the four-probe dc technique show that the conductivity of synthesized materials increases with the increment of both dopant concentration and temperature by the decrement of area specific resistances. The electrical conductivity of CSCFZ steadily increased with the increment of temperature which reached 42.76 Scm^{-1} at around 450°C .

1. Introduction

Using fossil fuels as energy sources cause environmental issues by affecting the atmosphere. These environmental issues affect human life and which leads to the innovation of alternative energy sources such as fuel cells. The usage of a safe, desirable, and clean energy carrier instead of fossil fuels has a substantial impact on diminishing air pollution [1]. Among fuel cells, SOFCs are the most attractive due to their fuel flexibility and high energy conversion efficiency on high operating temperatures [2, 3]. However, high operation temperature puts strict requirements on SOFCs component materials which lead to rapid degradation of the cells [2]. Research on the preparation and characterization of nanostructured materials is well known as a significant field in recent science and technology [4, 5]. These nanometer-

sized inorganic materials can represent an extensive range of optical and electrical properties [5]. The science and engineering of nanometer-sized materials is currently employed for the development of many scientific, industrial, ecological, and technological fields [6]. Biology, medicine, chemistry, pharmacy, agriculture, food industry, and materials science are the main fields that have been benefited from the great technological progress developed in nanoscience [6].

SOFCs convert the chemical energy of fuels straightforwardly into electrical energy with high efficiencies and minimal emissions. The three components of the fuel cell are an electrolyte layer in contact with a porous anode and cathode on either side [7]. To decrease the cost of SOFCs, there is significant interest in lowering the operating temperature of SOFCs [8]. SOFCs are based on O^{2-} conducting electrolytes and give a chance to use higher hydrocarbons

directly without a reforming step [9]. Porosity plays a great role in the overall cell performance. Perovskite-type cathode materials have been widely studied as cathode materials for SOFCs due to the possibility of both A-site and B-site doping [10]. Their structure offers wide flexibility to improve the properties of materials, such as catalytic activity, chemical stability, and thermal property [10].

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5080) has reached high oxygen permeability and was predictable to be structurally stable based on the evaluation of the Goldschmidt tolerance factor and is the main component in many following studies [11]. Although BSCF shows excellent electrochemical performance, it has a high thermal expansion coefficient (TEC) with the value of $20 \times 10^{-6} \text{K}^{-1}$ between 50°C and 1000°C which is problematic for cells using this cathode material due to a mismatched TEC with those of other cell components [12]. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) at 700°C was developed by using two sintering approaches. The reactive sintered body of hexagonal-phase BSCF obtained by the one-step process showed higher electrical conductivity of 6.35 Scm^{-1} at 500°C than the two-step sintered BSCF of electrical conductivity 4.15 Scm^{-1} [13].

Darb, in 2008, synthesized and characterized $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, among which the second composition has shown to be promising regarding physical properties [14]. Composite cathodes containing $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ have lower ASR than BSCF and LSCF cathodes [15]. The values of ASR are 0.46 and $2.77 \Omega \cdot \text{cm}^2$ at 700°C and 600°C , respectively, for the composite cathode $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ in 1 : 1 weight ratio. Compared to other cathode materials, the electronic conductivity of LSCF is very high with a maximum value of 215.58 Scm^{-1} at 823 K , whereas BSCF has a much lower electronic conductivity 14.87 Scm^{-1} at 773 K [16]. The TEC of BSCF is larger than the TEC of LSCF [17, 18]. Comparing with LSCF, BSCF is a better cathode material because it has the lowest surface resistance.

According to Yusof and Rahman, BSCF has been reported as a good and effective cathode material due to high conductivity, excellent oxygen transport, catalytic activity, and a potential candidate for a low-temperature solid oxide fuel cell (LT-SOFC) [19]. In their study, the nanocomposite cathode BSCF-samarium-doped ceria (SDC) was developed for LT-SOFC, and the behavior of the nanoceramic powders was examined [19]. The results obtained by their study confirm that selecting a suitable calcination temperature is important in eliminating secondary phases in the BSCF-SDC composite cathode and enhancing its properties. These secondary phases come from the reaction of the cathode and electrolyte because of a mismatch in the thermal expansion coefficient.

Perovskite $\text{Sr}_{1-x}\text{Ce}_x\text{CoO}_{3-\delta}$ ($0.05 \leq x \leq 0.15$) has been prepared by a sol-gel technique and studied for intermediate temperature solid oxide fuel cell cathodes [4]. As SOFC cathodes, $\text{Sr}_{1-x}\text{Ce}_x\text{CoO}_{3-\delta}$ materials have sufficiently high electronic conductivities and excellent chemical compatibility with SDC electrolyte [4]. At 1100 K , the oxygen atoms in $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_{3-\delta}$ show large and highly anisotropic displacement factors, suggesting significant ionic mobility

[20]. SOFCs have faced many challenges in commercializing them. Though most of the problems associated with performance and material issues have been resolved to a certain extent, commercial applications of SOFCs still suffer from high costs and high-temperature requirements [21]. Research studies regarding SOFCs are focused on the range $500\text{--}700^\circ\text{C}$; the slow cathode reaction in this range is the source of many energy losses [15].

Perovskite cathodes, LSCF and BSCF, have good electronic conductivity but their TECs are not matched with the electrolyte [22]. Replacing barium or lanthanum on A-site with cerium improves the problem by lowering the TEC of the cathode, but its electronic conductivity is not good because of the formation of unreacted secondary CeO_2 peak for a concentration of cerium $>15\%$ [23]. However, more concentration of cerium (50%) leads to giving good migration of charge carriers by creating more oxygen vacancies. However, if there is any unreacted Ce due to excess doping, it will be balanced by doping other elements in B-site.

The addition of high valence elements on B-site improves the cubic structure of the base material, which in turn increases electronic conductivity of the cathode [24]. Although there were many cathodes used (such as LSM, LSC, LSCF, and BSCF), the thermo-mechanical suitability between electrolyte and cathode can be improved by mixing cathode material with a new element or a small impurity such as zirconium and titanium [25]. Such composite cathode will have better electronic conductivity, and the overpotential of the cathode can be reduced by adding zirconium or titanium [25].

In this work, we prepared perovskite $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ (CSCFZ) oxide by a sol-gel technique. The crystal structure of $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ and the crystalline nature of the materials were investigated by X-ray diffraction (XRD). Its electrochemical performance as a cathode for SOFCs was examined in cathodic symmetrical cells. The relationship between the structure and properties of $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ as a cathode for SOFCs has been correlated, and the microscopic reason for the observed good performance has been revealed.

2. Experimental

2.1. Material Preparation Method. Cathode materials of $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ (CSCFZ) for $x = 0, 0.1, 0.15$, and 0.2 were synthesized by the sol-gel method. The raw materials and ingredients used are powders of the following AR-grade Sigma-Aldrich and Otto, India chemicals, as shown in Table 1.

Five grams of CSCFZ materials were chosen as target products. The individual nitrates of precursor powders were mixed by weighing properly with a digital microbalance and dissolved in distilled water. A stoichiometric amount of citric acid (1 : 1 ratio with a mole of nitrates), which plays the role of gelation agent, was dissolved in distilled water and mixed with the solution of metal nitrates by continuously stirring with a magnetic stirrer without heat. Then, the

TABLE 1: Chemicals and ingredients used.

S. no	Name of chemicals	Chemical formula	Suppliers	Purity (%)
1	Ferric nitrate	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Otto, India	>98
2	Cobalt (II) nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Otto, India	>99
3	Strontium nitrate	$\text{Sr}(\text{NO}_3)_2$	Otto, India	>99
4	Cerium (III) nitrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Sigma-Aldrich	>99.9
5	Zirconyl nitrate	$\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	Sigma-Aldrich	>99.9
6	Ammonia	NH_3	Otto, India	>99
7	Citric acid	$\text{C}_6\text{H}_8\text{O}_7$	Otto, India	>99
8	Methylcellulose	$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_x(\text{OCH}_3)_y$	Otto, India	>99

solution is stirred on a magnetic stirrer with a hot plate. To avoid the appearance of hydroxides and base salts at higher pH values, it is important checking the pH value is ~ 7 . The pH of the solution was adjusted by adding ammonia solution drop by drop using a saker and seeing the color of the pH paper by dropping a small amount of the solution by saker on it. After adjusting the pH of the solution, it was slowly heated for 6 hrs at 80°C over a temperature-controlled magnetic stirrer with a hot plate until the solution becomes a viscous solid called gel. During the reaction, the mixture is stirred continuously at high speed to avoid any agglomeration and for preparing the homogenous solution. After this, continue heating with reduced stirring speed for few minutes. Then, the gel is dropped from the beaker to the ceramic bowl and heated in a hot air oven for 7 hrs at 300°C until the gel becomes black ash. The presintered powders are grinded for 1 hr continuously with an agate mortar. The pre-sintering temperature was taken for 3 hrs at 800°C and final sintering was taken for 5 hrs at 950°C . The pellets were made by using a hydraulic press with stainless steel die by applying a load of 12 ton (having 9 mm diameter and 2 mm thickness). In the end, the prepared pellets were sintered at 950°C for 5 hrs in the furnace by putting it in a closed alumina crucible to get the final composition and the desired pure phase Perovskite before characterization and measurement.

2.2. Characterization. X-ray diffraction had been carried out to study the crystalline nature and phase purity of all four samples. The data was taken by Xpert Philips XRD using $\text{Cu-K}\alpha$ radiation with a wavelength of $\lambda = 0.1542 \text{ nm}$ at a scanning rate of $2^\circ/\text{min}$ with a Cu anode of 40 kV and 30 mA. Scanning was taken for 2θ values ranging from 20°C to 80°C . Scanning electron microscopy (SEM) is applied to investigate the grain morphology of prepared samples. A high-resolution SEM (ZEISS) was used to see the morphology of synthesized samples and to relate them with the physical behaviors of the particles used as a cathode material. In the study, the SEM analysis was carried out by using the sintered pellets of the samples. Electrical conductivity for all synthesized samples was measured by the four-probe (contacts) dc method.

2.3. Fabrication and Testing of Cells. Two grams of the powder was taken with 0.04 gram methylcellulose (2% of the powder) and grinded for 30 minutes continuously. SDC-based electrolytes were fabricated by the sol-gel technique and pelletized by a hydraulic press with stainless steel die by

applying a load of 12 ton (having 9 mm diameter and 2 mm thickness) and sintered at 1200°C for 5 hrs. Then, CSCFZ layers with submicron size were first coated on the surfaces of the electrolyte support using a screen-printing technique. Slurries of the cathode were fabricated using a mixture of α -terpineol and methylcellulose. Finally, the slurries of cathode materials were coated on top of the SDC layer and fired at 900°C for 5 hrs to study electrical properties. To verify the electrochemical performances of the cathodes, screen printed circular SDC with active areas of 0.741, 0.752, 0.743, and 0.7435 cm^2 per unit length for concentrations of $x = 0, 0.1, 0.15$, and 0.2 were constructed. The configuration of the cell was cathode and solid SDC electrolyte. For the electrochemical tests, Ag was pasted on the surface of the cathode as a current collection.

3. Results and Discussion

3.1. XRD Analysis. Crystallographic characterization of $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ ($x = 0, 0.1, 0.15, 0.2$) was carried out at room temperature. Figure 1 shows the XRD patterns of the as-synthesized $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ ($x = 0, 0.1, 0.15, 0.2$) at room temperature, which shows pure, well-crystallized perovskite phases, indexed in a cubic unit cell for both materials. The crystallinity nature of the materials increased as the doping of zirconium increases. The impurity peak (I) that came from unreacted CeO_2 minimized from the figures for high concentration of Zr and the sharpness of peaks increased. XRD reveals high-degree crystalline cathodes with cubic-type structure having the space group of Pm-3m. Ten symmetrical diffraction peaks were observed in the XRD spectra (111) for $2\theta = 28.47$, (200) for $2\theta = 33.26$, (211) for $2\theta = 41.35$, (220) for $2\theta = 47.63$, (221) for $2\theta = 49.99$, (311) for $2\theta = 56.50$, (222) for $2\theta = 59.28$, (321) for $2\theta = 66.17$, (400) for $2\theta = 68.48$, and (331) for $2\theta = 76.81$. This XRD pattern matches with standard single-phase cubic perovskite structure having the space group Pm-3m (JCPDS File No.: 109462) [26].

From XRD peaks, lattice parameters were calculated using UnitCellWin software. The mean crystallite size was calculated from the peaks broadening by using the Debey Scherrer equation from XRD data [27]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

The density of the samples increased as partial substitution of lighter elements with heavier elements increases

FIGURE 1: X-ray diffraction pattern for (a) $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ sample at concentration $x=0.15$ and (b) four all samples.

TABLE 2: Crystallite size, lattice parameter, and porosity of CeZr_0 , CeZr_1 , CeZr_2 , and CeZr_3 for $x=0, 0.1, 0.15$, and 0.2 , respectively.

S. name	Pos. ($2\theta^\circ$)	Mean crystallite size (D) (nm)	Lattice parameter (a) ($\text{\AA}$)	Porosity (%)
CeZr_0	28.4695	26.57	5.42293	9.93
CeZr_1	28.7046	18.14	5.40527	9.87
CeZr_2	28.7790	18.13	5.40213	9.50
CeZr_3	28.8054	18.12	5.40200	9.08

due to the concentration of dopant Zr on the B-site. As a result, the porosity of samples decreases by a small amount due to dopant. The materials are porous than earlier findings which are around 5% [28]. Even though porosity is one of the key criteria for SOFC cathode materials, the stability of material also plays a great role in the performances of SOFCs. The stability depends on the crystallinity nature of a material, and it was observed that the crystallinity nature of the samples increased as the concentration of dopant on the B-site increases. The variation of parameters is more likely a compensatory response of the crystal structure to accommodate dopants of different ionic sizes as compared to those of host ions which causes the shrinkage of a crystal lattice that leads to a decrease in the values of lattice constants.

3.2. SEM Analysis. As it is clearly seen from Figure 2, the crystal consists of a periodic arrangement of the unit cell into a lattice and exhibited complete densification with a presence of pores on the surface. The average grain sizes in each of the synthesized series get smaller when the dopant concentration increases as also evident from XRD data. Further reduction in average grain sizes of particles for doped samples in Figure 2 is owing to the incorporation of the dopant in perovskite cathodes, and it is in the range of 105.3025–183.025 nm. The average grain sizes of all the samples were calculated by the linear intercept technique.

3.3. Electrochemical Analysis. Electrical conductivities are the sum of electronic and oxygen ionic conductivity, owing to the co-presence of electron-hole pairs and oxygen vacancies. It is well known that the ionic conductivity is much lower than electronic conductivities in perovskite oxides. Therefore, it can be assumed reasonably that the measured conductivity values refer to the electronic conductivities alone [29].

The electrical conductivity of CSCF for $x=0$, steadily increased with temperature and then reached a level of approximately 15.62 Scm^{-1} at 450°C , while that of CSCFZ continuously increased with temperature up to 42.76 Scm^{-1} at the same temperature. The electrical conductivities are in a good range as shown in earlier findings [26], and it is much better than findings obtained by Yamaguchi et al. at 500°C [13] within a temperature range of interest ($250\text{--}450^\circ\text{C}$). Increment of temperature leads to high electronic conductivity of the cathode by decreasing the interface resistance, and this in turn leads to high electrochemical performance. Thus, the cathodic resistance of the materials would be lower.

The temperature dependence of electronic conductivity of all the prepared samples was presented in Figure 3 in the form of $\ln(\sigma T)$ versus $(10^3/T)$. The value of activation energies was calculated from the slope of the graphs and have a value of 0.83, 0.81, 0.77, and 0.72 eV for $x=0, 0.1, 0.15$, and 0.2 , respectively, which is less than the values of earlier findings of 1.15 eV [26, 30].

FIGURE 2: SEM micrographs for $\text{Ce}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ samples at concentrations of $x=0, 0.1, 0.15$, and 0.2 , respectively.

FIGURE 3: Electronic conductivities of all four samples CeZr_0 , CeZr_1 , CeZr_2 , and CeZr_3 for concentrations of $x=0, 0.1, 0.15$, and 0.2 , respectively.

FIGURE 4: Temperature dependence of area specific resistances (ASRs) of prepared samples.

TABLE 3: Electrical conductivities and area specific resistances of the prepared samples.

Temperature (°C)	σ (S cm^{-1})				ASR ($\Omega\cdot\text{cm}^2$)			
	CeZr ₀	CeZr ₁	CeZr ₂	CeZr ₃	CeZr ₀	CeZr ₁	CeZr ₂	CeZr ₃
250	9.51	10.41	11.95	13.52	0.1486	0.1428	0.1365	0.1295
300	10.67	12.45	14.86	17.19	0.1332	0.1275	0.1208	0.1152
350	11.13	13.31	17.08	21.44	0.1256	0.1201	0.1149	0.1095
400	12.25	17.49	21.78	30.79	0.1192	0.1132	0.1074	0.1025
450	15.62	22.26	32.74	42.76	0.1129	0.1076	0.1021	0.0980

An effective measure of the electrochemical performance of CSCFZ cathodes is area specific resistance (ASR) also called polarization resistances, which can be obtained from four-probe measurements on a symmetrical cell at various temperatures. The decrease in performance was followed by an increase in the ASR of the cell. Figure 4 shows that ASR values of CeZr₀, CeZr₁, CeZr₂, and CeZr₃ ($x=0, 0.1, 0.15$, and 0.2) cathodes were measured on temperature range of 250–450°C in air. ASR of CSCFZ cathodes is decreased with the rising of temperature and have values ranging from 0.098–0.1295 $\Omega\cdot\text{cm}^2$ to 250–450°C temperature range for concentration $x=0.2$. From this point of view, the concentration $x=0.2$ CSCFZ material can be considered as better cathodic candidates. The obtained ASR results are much lower than previous literature reported on the cells 1.74 $\Omega\cdot\text{cm}^2$ at 600°C [31–33], showing that this cathode can be used in the LIT-SOFCs and are in the range of 0.07–0.3 $\Omega\cdot\text{cm}^2$ [24]: where s is DC conductivity, t is the thickness of the sample, R is the resistance of the sample, and A is the area of the sample [34].

$$\text{ASR} = R_{\text{interface}} * A,$$

$$\sigma = \frac{t}{RA}, \quad (2)$$

As it is clearly seen from Table 3, electronic conductivity is increased with the increment of both doping concentration

and temperature. As it was seen from X-ray diffraction patterns, the presence of a secondary phase (CeO₂) leads to low electrical conductivity because the appearance of this additional phase (peak) leads to an increase in the overall resistance of the button cell. Therefore, CSCFZ at $x=0$ concentration exhibits the poorest performance among all the cathode materials prepared and characterized.

4. Conclusions

Ce_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{1-x}Zr_xO_{3-δ} (CSCFZ) powders for $x=0$ and ($0.1 \leq x \leq 0.2$) in a step sizes increment of 0.05 had been synthesized by the sol-gel method and characterized to explore their properties to use as a cathode material for low intermediate temperature solid oxide fuel cells (LIT-SOFCs). The crystal structure, microstructure, thermal properties, and electronic conductivity of the synthesized samples have been determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and the four-probe dc technique. The XRD result gives that all samples are single phases with a cubic perovskite-type structure with an average crystallite size of 26.57 nm, 18.14 nm, 18.13 nm, and 18.12 nm for $x=0, 0.1, 0.15$, and 0.2 , respectively. From the results obtained by XRD data, the lattice parameters of the prepared samples were 5.42293 Å, 5.40527 Å, 5.40213 Å, and 5.40200 Å. The samples were porous with porosities of 9.93%, 9.87%, 9.50%, and 9.08%. Results of SEM

micrograph show that the crystals consist of a periodic arrangement of the unit cell into a lattice and exhibit complete densification with a presence of pores in the surface with the average grain sizes ranging from 105–183 nm. The obtained results from the four-probe show ASR is in the range of $0.07\text{--}0.3\Omega\cdot\text{cm}^2$ and decreases with the increment of temperature and dopant concentration which leads to the increase of electronic conductivity of the prepared cathode materials in the range of $9.51\text{--}42.76\text{ Scm}^{-1}$ for a temperature range of (250–450°C). The increase of zirconium concentration has a positive effect on electronic conductivity by minimizing/removing the appearance of the unwanted secondary phase (CeO_2).

Data Availability

The data used to support the findings of this study are included within the article and are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to express their gratitude to the department of physics and chemistry of Osmania University and central university, Hyderabad, India, for allowing to use their laboratory facilities.

References

- [1] S. Zinatloo-Ajabshir, M. S. Morassaei, O. Amiri, and M. Salavati-Niasari, “ $\text{Nd}_2\text{Sn}_2\text{O}_7$ nanostructures: green synthesis and characterization using date palm extract, a potential electrochemical hydrogen storage material,” *Ceramics International*, vol. 46, pp. 17186–17196, 2020.
- [2] S. Moshtaghi and S. Z.-A. Salavati-Niasari, “Preparation and characterization of BaSnO_3 nanostructures via a new simple surfactant-free route,” *Journal of Materials Science: Materials in Electronics*, 2015.
- [3] Y. Gong, C. Sun, Q.-a. Huang, J. A. Alonso, and M. T.-D. Chen, “Dynamic octahedral breathing in oxygen-deficient $\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ perovskite performing as a cathode in intermediate-temperature SOFC,” *Inorganic Chemistry*, vol. 55, pp. 3091–3097, 2016.
- [4] W. Yang, T. Hong, S. Li, Z. Ma, C. Sun, and C. X. Chen, “Perovskite $\text{Sr}_{1-x}\text{Ce}_x\text{CoO}_{3-\delta}$ ($0.05 \leq x \leq 0.15$) as superior cathodes for intermediate temperature solid oxide fuel cells,” *ACS Applied Materials & Interfaces*, vol. 5, pp. 1143–1148, 2013.
- [5] M. Masjedi-Arani and M. Salavati-Niasari, “A simple sonochemical approach for synthesis and characterization of Zn_2SiO_4 nanostructures,” *Ultrasonics Sonochemistry*, vol. 29, pp. 226–235, 2016.
- [6] M. Amiri and M. S.-N. Akbari, “Magnetic nanocarriers: evolution of spinel ferrites for medical applications,” *Advances in Colloid and Interface Science*, vol. 265, pp. 29–44, 2019.
- [7] S. Stefan, “Yttria-stabilized zirconia and gadolinia-doped ceria thin films for fuel cell applications,” pp. 0345–7524, 2014.
- [8] R. M. Ormerod, “Solid oxide fuel cells,” *Chemical Society Reviews*, vol. 32, pp. 17–28, 2003.
- [9] S. McIntosh and R. J. Gorte, “Direct hydrocarbon solid oxide fuel cells,” *American Chemical Society*, vol. 104, pp. 4845–4865, 2004.
- [10] H. Yokokawa and T. Horita, *High Temperature Solid Oxide Fuel Cells Fundamentals, Design and Applications*, Vol. 119, Elsevier Science, Amsterdam, Netherlands, 2003.
- [11] Z. P. Shao, W. S. Yang, Y. Cong, H. Dong, J. H. Tong, and G. X. Xiong, “Operation of perovskite membrane under vacuum and elevated pressures for high-purity oxygen production,” *Membrane Science*, vol. 345, pp. 47–52, 2001.
- [12] B. Wei, Z. Lü, X. Huang, J. Miao, X. Sha, X. Xin et al., “Crystal structure, thermal expansion and electrical conductivity of perovskite oxides $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.3 \leq x \leq 0.7$),” *Journal of the European Ceramic Society*, vol. 26, pp. 2827–2832, 2006.
- [13] Y. Yamaguchi, H. Sumi, H. Shimada, T. Yamaguchi, and K. Nomura, “Reactive-sintering of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ using alkaline earth peroxides for low-temperature synthesis,” *Journal of the Ceramic Society of Japan*, vol. 125, pp. 681–685, 2017.
- [14] M. Darab, “Synthesis and characterization of nanostructured cathode material (BSCF) for solid oxide fuel cells,” M.S. thesis, Royal Institute of Technology (KTH), Stockholm, Sweden, 2008.
- [15] M. Mosialek, A. Kedra, M. Krzan, E. Bielanska, and M. Tatko, “ $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ composite cathode for solid oxide fuel cell,” *Archives of Metallurgy and Materials*, vol. 61, pp. 1483–1488, 2016.
- [16] A. Jun, S. Yoo, O.-h. Gwon, J. Shin, and G. Kim, “Thermodynamic and electrical properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ for intermediate-temperature solid oxide fuel cells,” *Electrochimica Acta*, vol. 89, pp. 372–376, 2013.
- [17] W. Zhou, R. Ran, and Z. Shao, “Progress in understanding and development of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -based cathodes for intermediate temperature solid-oxide fuel cells: A review,” *Journal of Power Sources*, vol. 192, pp. 231–246, 2009.
- [18] M. Kuhn, S. Hashimoto, K. Sato, K. Yashiro, and J. Mizusaki, “Thermo-chemical lattice expansion in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$,” *Solid State Ionics*, vol. 241, pp. 12–16, 2013.
- [19] U. Yusof and H. Rahman, “Properties of BSCF-SDC composite cathode powder for low temperature solid oxide fuel cell,” *Journal of Physics: Conference Series*, vol. 1082, Article ID 012029, 2018.
- [20] W. Yang, H. Zhang, C. Sun, L. Liu, J. A. Alonso, and M. T.-D. Chen, “Insight into the structure and functional application of the $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_{3-\delta}$ cathode for solid oxide fuel cells,” *Inorganic Chemistry*, vol. 54, pp. 3477–3484, 2015.
- [21] N. Akhtar, *Single-Chamber Solid Oxide Fuel Cells: Modeling and Experiments*, University of Birmingham Research Archive, Birmingham, UK, 2010.
- [22] A. Giuliano, M. P. Carpanese, D. Clematis, M. Boaro, A. Pappacena, F. Deganello et al., “Infiltration, overpotential and ageing effects on cathodes for solid oxide fuel cells: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ versus $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$,” *Journal of the electrochemical Society*, vol. 164, pp. F3114–F3122, 2017.
- [23] H. Choi, A. Fuller, J. Davis, C. Wielgus, and U. S. Ozkan, “Ce-doped strontium cobalt ferrite perovskites as cathode catalysts for solid oxide fuel cells: Effect of dopant concentration,” *Applied Catalysis B: Environmental*, vol. 127, pp. 336–341, 2012.

- [24] N. A. Baharuddin, A. Muchtar, and M. R. Somalu, "Short review on cobalt-free cathodes for solid oxide fuel cells," *International journal of hydrogen energy*, vol. 4, p. 97, 2016.
- [25] D. R. Sharma, P. V. Rao, M. N. Reddy, and D. Srikanth, "Synthesis and Characterization of $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Zr}_x\text{O}_{3-\delta}$ (BSCF) Nanoceramic Cathode Powders by Sol-Gel Process for Solid Oxide Fuel Cell," *Materials Today: Proceedings*, vol. 2, pp. 4442–4450, 2015.
- [26] Z. Yang, A. S. Harvey, A. Infortuna, J. Schoonman, and L. J. Gauckler, "Electrical conductivity and defect chemistry of $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ perovskites," *Journal of Solid State Electrochemistry*, vol. 15, pp. 277–284, 2011.
- [27] M. J. Iqbal, Z. Ahmad, Y. Melikhov, and J. C. Nlebedim, "Effect of Cu-Cr co-substitution on magnetic properties of nanocrystalline magnesium ferrite," *Journal of Magnetism and Magnetic Materials*, vol. 324, pp. 1088–1094, 2012.
- [28] D. R. Sharma and P. V. Rao, "Synthesis and characterization of $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Ti}_x\text{O}_{3-\delta}$ (BSCF) cathode for solid oxide fuel cell," *International Journal of Scientific and Research Publications*, vol. 5, pp. 6-7, 2015.
- [29] A. A. Samat, A. A. Jais, M. R. Somalu, N. Osman, A. Muchta, and K. L. Lim, "Electrical and electrochemical characteristics of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ cathode materials synthesized by a modified citrate EDTA sol-gel method assisted with activated carbon for proton-conducting solid oxide fuel cell application," *Journal of Sol-Gel Science and Technology*, 2018.
- [30] P. R. Kautkar, S. C. Shirbhate, and S. A. Acharya, "Study on structural refinement and electrochemical behavior of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC)," *AIP Conference Proceedings*, vol. 1953, Article ID 090057, 2018.
- [31] M. N. Sithole, B. Omondi, and P. G. Ndungu, "Synthesis and characterization of $\text{Ce}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ perovskite material: potential cathode material for low temperature SOFCs," *Journal of Rare Earths*, vol. 35, p. 389, 2017.
- [32] C. S. Devi and G. Prasad, "Development of nano-structured and nano porous BSCF cathode for low temperature solid oxide fuel cell application," *Transactions of the Indian Ceramic Society*, vol. 77, pp. 67–72, 2018.
- [33] C. Sun and R. H. Roller, "Cathode materials for solid oxide fuel cells: a review," *Journal of Solid State Electrochemistry*, vol. 14, pp. 1125–1144, 2010.
- [34] B.S. Nagraire and S. P. Shaikh, "Influence of preparative techniques on microstructure and electrochemical properties of $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (BSCF3764) cathode for IT-SOFC," *Journal of International Academy of Physical Sciences*, vol. 15, pp. 239–254, 2011.