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Structure and thermal properties of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–SDC carbonate composite cathodes for intermediate- to low-temperature solid oxide fuel cells

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Abstract

The structure and thermal properties of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–SDC carbonate (LSCF–SDC carbonate) composite cathodes were investigated with respect to the calcination temperatures and the weight content of the samarium-doped ceria (SDC) carbonate electrolyte. The composite cathode powder has been prepared from $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and SDC carbonate powders using the high-energy ball milling technique in air at room temperature. Different powder mixtures at 30 wt%, 40 wt% and 50 wt% of SDC carbonate were calcined at 750–900 °C. The findings indicated that the structure and thermal properties of the composite cathodes were responsive to the calcination temperature and the content of SDC carbonate. The absence of any new phases as confirmed via XRD analysis demonstrated the excellent compatibility between the cathode and electrolyte materials. The particle size of the composite cathode powder was ∼0.3–0.9 μm having a surface area of 4–15 $m^2\,g^{-1}$. SEM investigation revealed the presence of large particles in the resultant powders resulting from the increased calcination temperature. The composite cathode containing 50 wt% SDC carbonate was found to exhibit the best thermal expansion compatibility with the electrolyte.

Keywords: A. Calcination; B. Composites; C. Thermal expansion; E. Fuel cells

1. Introduction

Studies on improving electrode materials have increased over the past few decades. In particular, enhancing the properties of cathodes for solid oxide fuel cells (SOFCs) has attracted considerable interest. The operating temperature of SOFCs needs to be lowered to stabilize their performance and make them become commercially feasible. Lowering the operational temperature below 700 °C can prolong the lifetime of all SOFC components. Previous reports indicated that key improvements in cell performance can be realized by investigating and enhancing novel or as-developed cathode materials [1–5].

One approach to improving low-temperature cathode performance involves the development of composite cathode materials. In such a case, the electrolyte material added to the electrode material contributes to the increase in the triple phase (air/electrode/electrolyte) regions where the electrochemical reactions occur. This approach has been applied to mixed ionic and electronic conductors such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF6428). LSCF6428 has been recognized as one of the promising cathode materials for SOFCs. The addition of LSCF to samarium-doped ceria (SDC) electrolytes has been proven to produce a high-performance potential cathode for intermediate-temperature SOFCs [3,5–8].

Recently, an innovative solid carbonate-oxide composite that performed well at low temperatures of 400–600 °C was discovered [9–12]. Therefore, the combination of LSCF6428

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with SDC carbonates (SDCC) is expected to yield outstanding properties as composite cathode materials for intermediate- to low-temperature SOFCs (IT–LTSOFCs). Thus far, these systems have been studied in terms of their electrochemical properties and the fabrication technique. However, other issues concerning the development of these composite cathodes are still open for investigation. Such issues include the effect of calcination temperature as well as electrolyte fraction on the structure and thermal expansion properties of composite cathodes. The composite cathode properties are also influenced by the powder fabrication method. From the conventional mixing method to more advanced techniques such as the polymerizable complex method, infiltration or impregnation processes have been utilized in the development of composite cathodes [4,7,13,14]. Among currently available methods, the milling method is one of the simplest techniques used to produce composite powders. This method normally employs a low-energy milling force and a longer milling time [3–5].

In the present study, composite cathode powders comprising intimate mixtures of the electrically conducting electrode material LSCF6428 and the nanoscale ionically conducting electrolyte material SDCC were developed. The high-energy ball-milling technique was used to prepare the powders within a short milling time. The structural and thermal properties of the composite cathodes were investigated with respect to the calcination temperature and weight ratio of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode to the SDC carbonate electrolyte.

2. Experimental procedure

2.1. Materials and specimen preparation

The starting materials used were a commercial LSCF6428 powder (particle sizes = 0.3–0.6 μm; Sigma–Aldrich) and an in-house-developed SDCC powder. A mixture of 80 wt% SDC nanopowder (Sigma–Aldrich) and 20 wt% carbonates (67 mol% Li_2CO_3:33 mol% Na_2CO_3) [15,16] was prepared by conventional solid state reaction. The SDC, Li_2CO_3 and Na_2CO_3 powders were mixed and ball-milled for 24 h in order to obtain homogenize composite powder. The mixture was oven-dried and then heat-treated at 680 °C for 40 min.

Subsequently, 30–50 wt% SDCC powder was mixed with the LSCF6428 powder. Hereinafter, the LSCF–SDCC composites were designated as LSCF–SDCC55 (55 means 50 wt% LSCF and 50 wt% SDCC), LSCF–SDCC64, and LSCF–SDCC73. The composite cathode powders were ball-milled (Fritsch Pulverissete 6, Germany) in ethanol using zirconium oxide balls and bowls as grinding media. The milling was performed in air at room temperature at a rotational speed of 550 rpm for 2 h, and the milled powders were dried in air for overnight. The required fine and homogeneous particles from the resulting milled powder have been achieved as shown in Fig. 1. The dried powders were then ground in an agate mortar and sintered in air in an electrical furnace at 750, 800, 850, and 900 °C for 2 h with a heating rate of 10 °C min^{-1} to get phase perovskite materials.

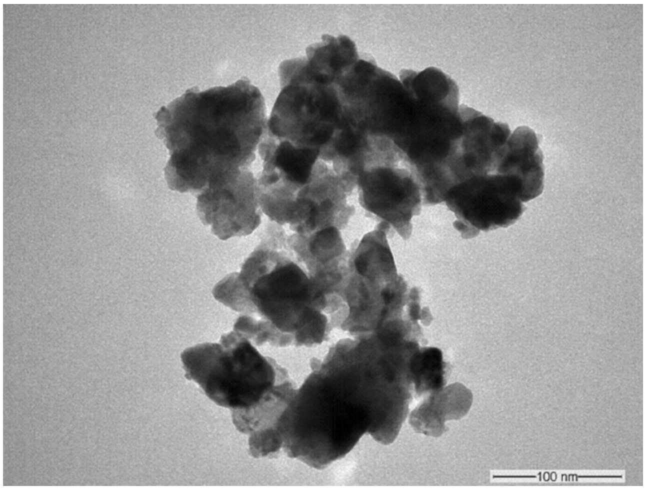

Fig. 1. TEM image of composite powder LSCF–SDCC55 after milling.

2.2. Characterization methods

Phase purity and crystalline structure analyses of each composite cathode powder were carried out using a Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) at room temperature. The diffraction patterns were collected by step scanning of 0.02° in the 2θ range from 20° to 80°. The weight loss of the uncalcined LSCF–SDCC powders as a function of temperature was obtained via thermogravimetric (TG) measurements up to 900 °C in air at a heating rate of 10 °C min^{-1} (model TGA/SDTA 851, Mettler, Switzerland). Thermal expansion coefficients (TECs) were measured using cylindrical LSCF–SDCC samples upon heating in air from room temperature to 800 °C by a dilatometer (Netzsch DIL 402C, Germany). Alumina was used as the reference and the heating rate was 5 °C min^{-1}. A micromeritics surface area analyzer (model ASAP 2010, USA) based on the Brunauer–Emmett–Teller (BET) principle was used to measure specific surface areas. The particle sizes of the powders were characterized using a laser particle size analyzer (Zetasizer Nanoseries ZS, Malvern, UK). The morphology of the calcined powders was studied by field emission scanning electron microscope (Zeiss Supra 55VP, Germany) coupled with the energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. XRD analysis

Fig. 2 displays the X-ray diffraction (XRD) patterns of the LSCF–SDCC composite powders with different compositions calcined at 800 °C. Meanwhile, Fig. 3 shows the X-ray spectra of composite cathodes LS–SDCC64 at various calcinations temperatures. The composite cathodes are assignable to two perovskite phases of LSCF6428 and SDCC. No remarkable secondary constituent from the resultant LSCF–SDCC powders is detected within the XRD sensitivity. The introduction of carbonates into SDC does not influence its structure as the composite cathode powders are able to maintain their own

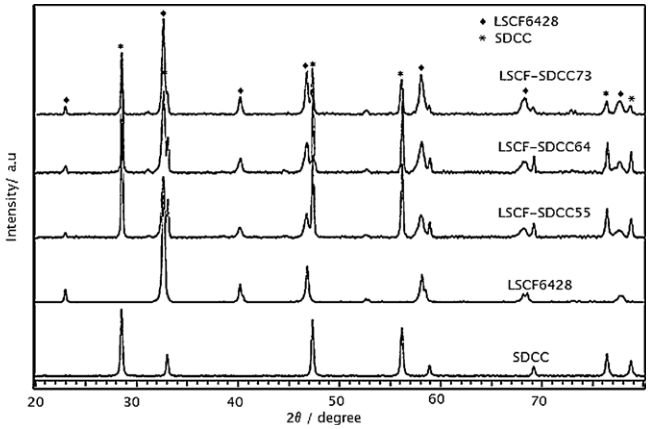

Fig. 2. XRD patterns of SDCC, LSCF6428, and LSCF–SDCC powders calcined at 800 °C.

structures after mixing and calcination. The other LSCF–SDCC composite powders with different composition and calcinations temperatures also illustrated similar patterns as LSCF–SDCC64 that has been discussed above. Comparable results were observed in previous studies [5,10,11,15]. Given the capability of the LSCF–SDCC in producing porous composite cathodes at low calcination temperatures [3,5,17,18] and its chemical compatibility, it is expected to be a suitable composite cathode for IT–LTSOFCs.

3.2. Thermal property analysis

The TG weight losses of the prepared LSCF–SDCC composite cathodes upon heating in air are plotted versus temperature in Fig. 4. The amount of weight loss increases with increased SDCC content in the composite cathodes. However, all LSCF–SDCC composite cathode compositions only show minor weight losses (below 9.0%) up to 900 °C. Information from the TG curves helps ensure that the selected calcination temperatures (from 750 to 900 °C) remain below the decompositional temperature of the composite cathodes.

The technical TEC values for the LSCF–SDCC composite cathodes at low temperatures (100–550 °C) are shown in Table 1. The trend of the TEC results demonstrates that increased electrolyte amounts in the composite cathode bring the TEC of the cathode closer to that of the electrolyte. This observation is supported by similar findings from other studies [5,10]. According to Letilly [19], a TEC difference of less than 10% between the cathode and the electrolyte is suitable for mechanical compatibility to prevent delamination during

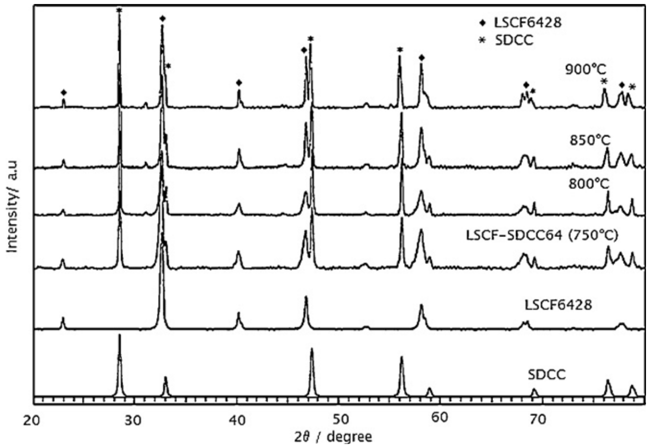

Fig. 3. XRD patterns of SDCC, LSCF6428, and LSCF–SDCC64 powders calcined at different temperatures.

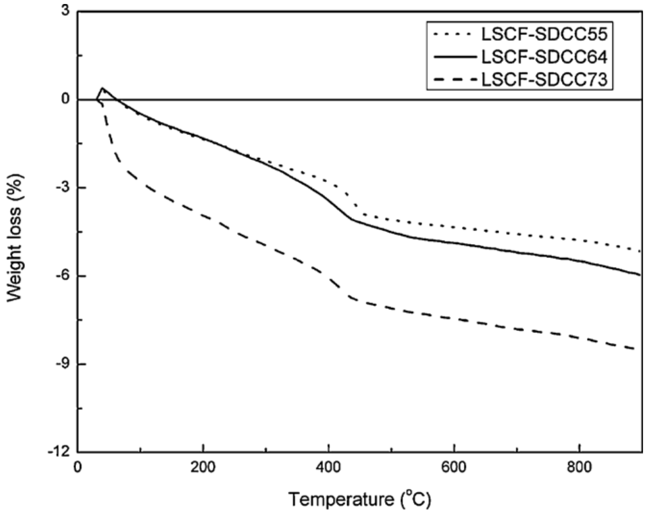

Fig. 4. TG weight loss of various LSCF–SDCC composite cathodes as a function of temperature.

Table 1
Average TEC values at low temperature range for SDCC, and LSCF–SDCC composite cathodes.

Calcination temperature (°C)	TEC ($\times 10^{-6}$ K^{-1}) (100–550 °C)			
	SDCC	LSCF–SDCC55	LSCF–SDCC64	LSCF–SDCC73
	[a]3.36	–	–	–
750	–	3.66	5.68	5.84
800	–	3.13	3.81	4.59
850	–	3.59	6.15	5.80
900	–	3.21	3.22	5.28

[a] The SDCC powder for TEC analysis was calcined at 600 °C for 2 h.

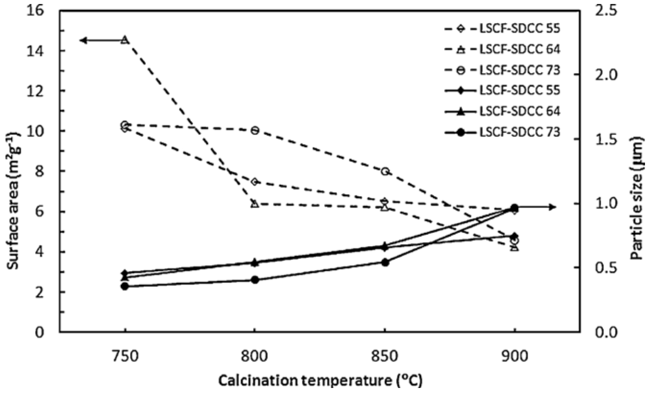

Fig. 5. Surface area and particle size as a function of calcination temperature for various compositions of composite cathode powder.

processing or applications at elevated temperatures. Based on this criterion, the LSCF–SDCC55 composite cathode with TEC difference between 4 and 9% most appropriately matches the SDCC electrolyte in terms of the TEC value.

3.3. Particle size and microstructure analysis

The surface areas of the calcined LSCF–SDCC composite cathodes powder were determined using the BET principle. The measured surface areas of the developed composite powders are in the range of 4–15 $m^2\ g^{-1}$. The obtained surface areas are comparable with those of other composite cathodes from previous research [4]. Fig. 5 shows the influence of the calcination temperature on the surface area and particle size of the composite cathode powder. The particle sizes of both types of composite powders increase with increased calcination temperature. According to the theory of sintering of ceramic materials, particle growth during the calcination process contributes to increased powder particle size and decreased surface area [20].

A similar phenomenon was reported by Seabaugh and Swartz [4]. In addition, Fig. 5 shows that the composite powder

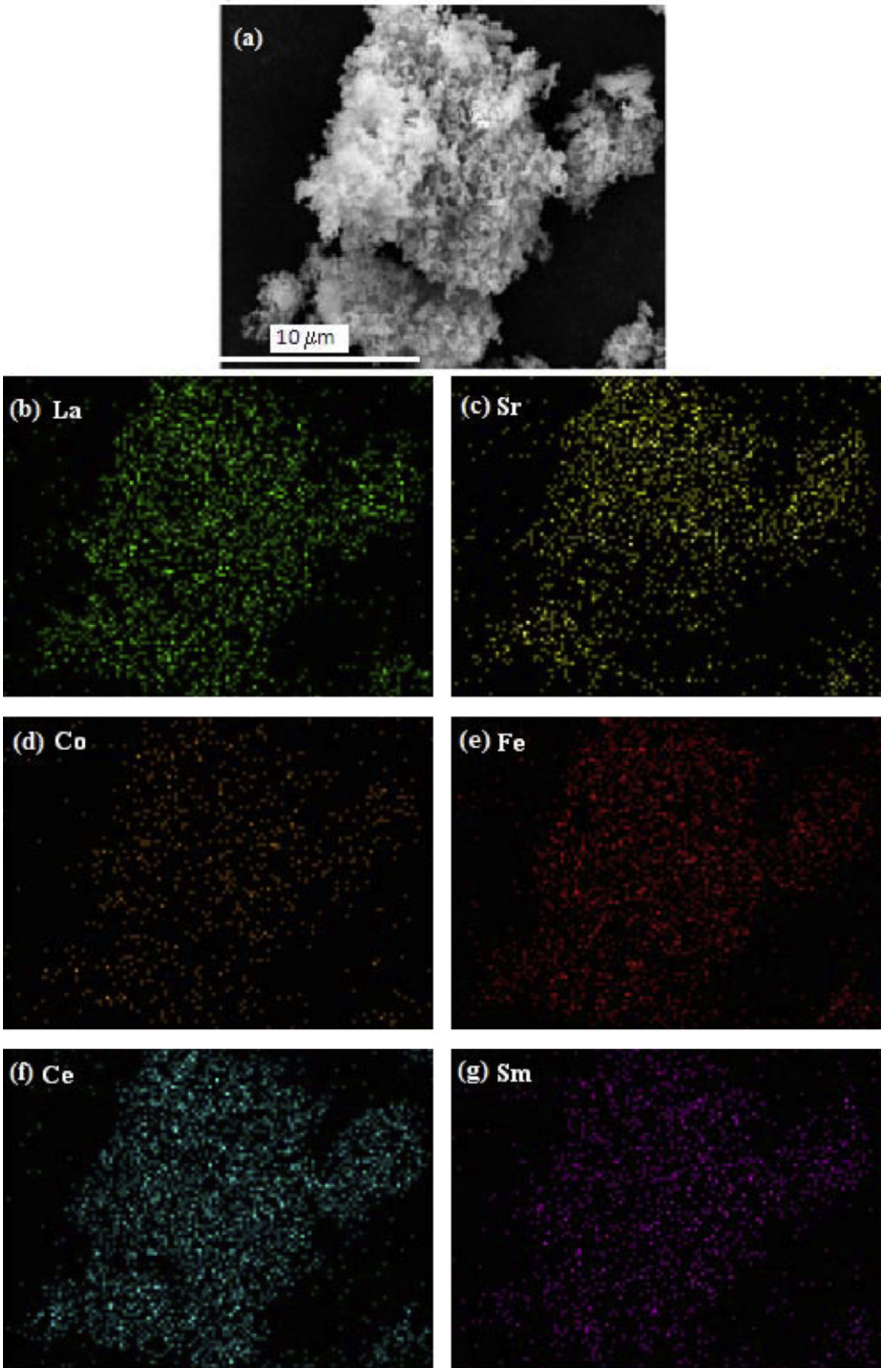

Fig. 6. Distribution of elements in the LSCF–SDCC55 composite cathode powder calcined at 750 °C via EDS mapping.

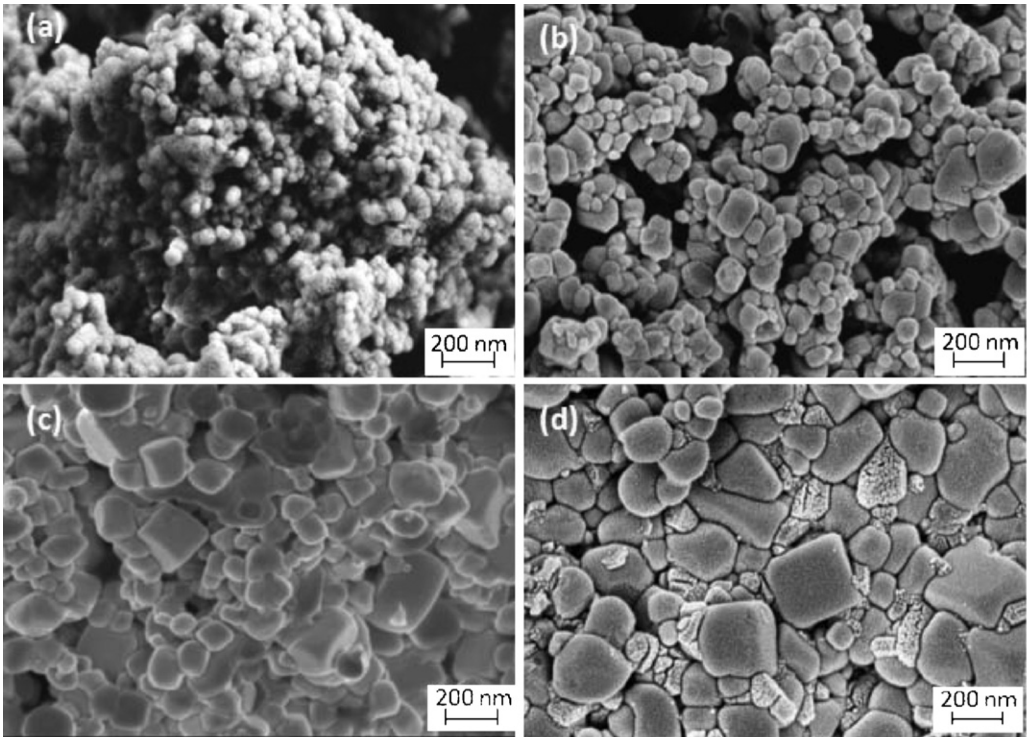

Fig. 7. FESEM micrographs of the LSCF–SDCC55 composite cathode powder calcined at (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C.

with a higher SDCC amount (LSCF–SDCC55) has slightly larger particle sizes compared with the others. The particle size difference among these composite powders is mostly attributed to the coating of the $(Li/Na)_2CO_3$ amorphous phase over the electrolyte and electrode particles [9,10,15].

The homogeneity of the composite cathode powder from the milling process is shown in Fig. 6. The energy-dispersive X-ray mapping images prove that all the major elements are well distributed among the composite powders. Figs. 7 and 8 illustrate the morphology of the LSCF–SDCC composite

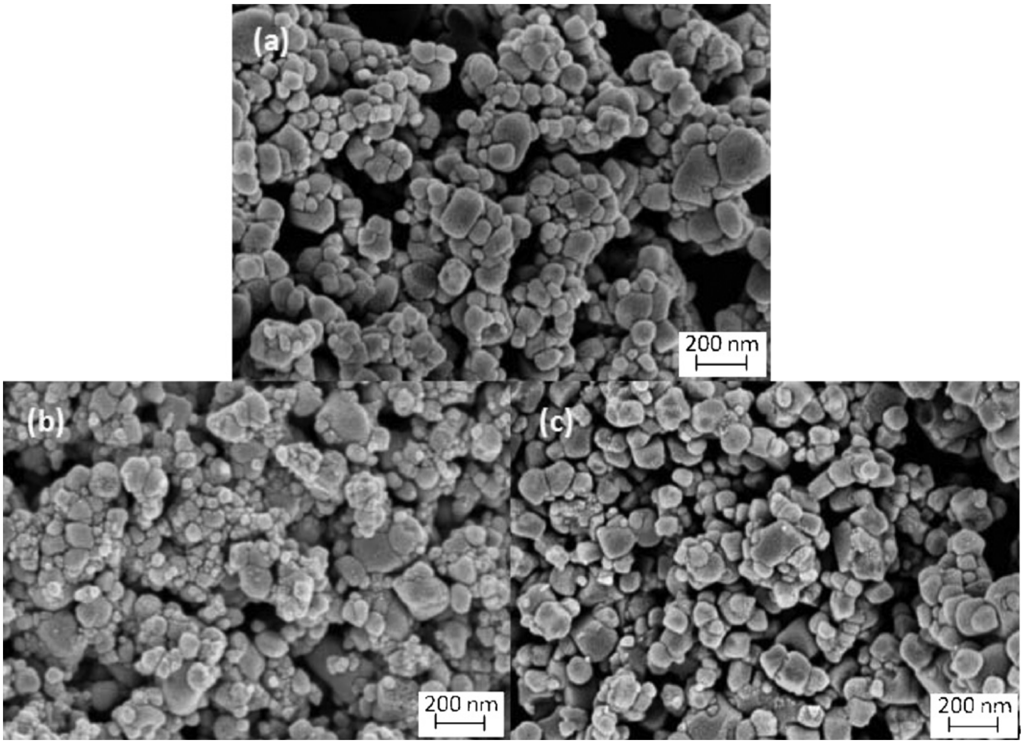

Fig. 8. FESEM micrographs of various composite cathode powder (a) LS–SDCC55, (b) LS–SDCC64 and (c) LS–SDCC73 calcined at 800 °C.

cathode powders. Obviously, calcination temperatures strongly influence the particle size of the resultant composite powders. The SEM micrographs support the analysis of the particle sizes. The equiaxial shape of the obtained LSCF–SDCC composite cathode powders is attributed to the ball to powder weight ratio. A ball to powder ratio equal or higher than 10:1 tends to produce equiaxed-shaped particles after the milling process [21]. Such an equiaxed particle shape is one of the most desirable powder characteristics in advanced ceramics applications [20]. However, the differences in the compositions of the composite cathodes do not significantly influence the cathode properties, especially the particle size of the resultant powders.

4. Conclusions

Homogenously mixed, fine-powdered LSCF–SDCC composite cathodes have been successfully developed via the high-energy ball-milling technique. The structure and thermal properties of the cathodes have been studied with regard to the calcination temperature and the weight fraction of the SDCC electrolyte. The results indicate a good compatibility of the materials used in the composite cathodes because no chemical reaction product is observed after the calcination process between 750 °C and 900 °C. The particle size and morphology of the composite powders are influenced more by the calcination temperature. On the other hand, the thermal expansion properties are sensitive to the fraction of the SDCC electrolyte. A higher electrolyte amount in the composite powders brings the TEC values of the composite cathodes closer to the electrolyte. Overall, the findings in the present work indicate the potential of LSCF–SDCC composites as cathode materials for SOFCs. More detailed investigations of the electrochemical and electrical conductivities of these composite cathodes are expected to be conducted in the future.

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