Morphological and Physical Behaviour of LSCF-SDCC-Ag Composite Cathode with the Incorporation of Ag as an Additive Element

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Abstract. The composite cathode, lanthanum strontium cobalt ferrite-samarium-doped ceria carbonate-argentum (LSCF–SDCC–Ag), was developed and investigated for low-temperature solid oxide fuel cell (LTSOFC) applications. This research studied the effect of Ag on the development and properties of the composite cathode. The composite cathode powders, LSCF–SDCC–Ag with an Ag addition of 1–5 wt% were developed via high energy ball milling technique, and all prepared pellets were sintered at 500, 550, and 600 °C. The morphological properties of the composite cathode powders were observed via FESEM micrograph, and the average particle sizes of the composite powders were measured via SmartTiff Software. The total porosity (%) of the LSCF–SDCC–Ag composite cathode pellets was determined using the Archimedes method. The FESEM micrograph revealed that the obtained composite cathode powder is homogeneous, with particle sizes of 100–200 nm. The particle size of the LSCF–SDCC–Ag cathode increased with the increase of Ag content. Meanwhile, the porosity decreased in value with the increase of the Ag content and the sintering temperature. The porosity percentage range from 26.6% to 33.8%.

1. Introduction

The solid oxide fuel cell (SOFC) is an electrochemical energy conversion device that delivers high electrical efficiency and significant environmental friendliness in terms of fuel flexibility. It is also clean and efficient with more than 70% with fuel regeneration electric power generation. A SOFC produces useful electricity from the reaction via the diffusion of oxide ions (or protons) through an ion acting between solid electrolyte layers [1–2]. Initial research in SOFCs focused mostly on high temperatures between 800 and 1000 °C. Reliability issues at high temperature have caused a shift in SOFC research towards operation at low temperatures (LT) to intermediate temperatures (IT), that is, from 400 °C to 750 °C. However, a reduction in operating temperature reduces the efficiency of the cathode elements, as it leads to the increase in cathode polarization resistance causes a substantial performance decline [3]. Designing a high-performance electrode with low polarization resistance (such as by using a composite cathode) is a potential solution for the aforementioned problems [4]. One of the method to improve low-temperature cathode performance involves the development of composite cathode materials. Recently, numerous SOFC researchers have studied issues associated
with operational temperature. They have presented significant solutions regarding cathode material selection, synthesis, and processing.

Perovskite-type materials have been widely used as cathode materials in SOFCs. A key characteristic of the perovskite structure is its ability to conduct both electrons and ionic species, thus leading to them being designated as mixed electronic and ionic conductors (MIECs) [5]. MIEC materials from rare earth cobalt oxide groups include La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), one of the promising cathode materials with good electrical conductivity, a good thermal expansion coefficient, and a good melting point [6]. The universal properties of MIECs include good ionic and electronic conductivity. Their excellent conductivity property enhances the triple phase boundary (TPB), which holds the reactive site at the cathode. This phenomenon may account for the improved electrochemical performance of the SOFC [7].

Additionally, an electrolyte composite known as samarium doped ceria (SDC) carbonate (SDCC) was found to perform well at low temperatures (400–600 °C). The incorporation of SDCC into LSCF was reported to dramatically affect the electrochemical potential of IT–LTSOFC cathode. The use of binary carbonate ((Li/Na2)CO3) together with SDC is to overcome ionic conductivity issues, in which the LSCF–SDCC composite cathode was reported to be efficient as LTSOFC. It has been proven to yield outstanding properties [8–10]. Nevertheless, ceria-based electrolyte systems have contributed to an increase in the power outputs of LTSOFCs. The use of SDC electrolytes is believed to improve the performance of LSCF–SDCC composite cathode because carbonates universally exhibit good compatibility with many composite cathode powders.

The evaluation of SOFCs has significantly enhanced the performance of composite cathode powders through the incorporation of metallic elements such as silver (Ag), platinum (Pt), palladium (Pd), and cuprum (Cu). Given its superior electronic conductivity, high catalytic activity, substantial oxygen solubility, and mobility, Ag is considered the most suitable candidate as a cathode material in LTSoFC applications [11–12]. Moreover, the use of this metal also improves the cathode microstructure, as the melting point of Ag is 961 °C. This advantage may aid the sintering behavior of the LSCF–SDCC–Ag composite cathode. This research work focuses on developing the composite cathode, LSCF–SDCC–Ag, to suit LTSoFC applications. Further investigations are on the effect of Ag addition to the morphological and characteristic of the composite cathode LSCF–SDCC materials.

2. Materials and Methods
A commercial LSCF powder (LSCF6428; KCeracell, Korea), self-fabricated SDC, and a binary carbonate (SDCC) powder were used. A mixture of SDC and binary carbonate was ball-milled for 24 hours before being dried overnight in an oven and undergoing calcination at 680 °C. The composite cathode powder of LSCF–SDCC was prepared with a weight percentage ratio of 50:50 using high energy ball milling (HEBM) techniques with propanol as the solvent medium. The obtained powder was then ground using an agate mortar and calcined in a furnace at 750 °C. For the preparation of LSCF–SDCC–Ag, a dry mixing method of 100 rpm was employed with the addition of 1–5 wt% Ag powder. The LSCF–SDCC–Ag composite cathode pellets were fabricated via a uniaxial press using a constant pressure of 46 MPa followed by a sintering process at temperatures ranging from 500–600 °C. To obtain the desired porosity ranging from 20%–40%, the sintering temperatures used in this study were lower than the temperature used for calcinations.

Next, the morphology of the composite cathode LSCF–SDCC without Ag content and the LSCF–SDCC–Ag (1–5 wt%) were observed via FESEM. The average particle size measurements were obtained using SmartTiff Software (Version V02.01, Carl Zeiss Microscopy Limited) based on the exact scale on the FESEM image. By using the Mettler Toledo machine, the Archimedes method was employed to measure the porosity of the composite cathode sintered pellet. The porosity measurement methods were based on the standard ASTM C20-00 (Standard test Method for Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water), with several modifications for compatibility with the composite cathode
pellet samples. Composite cathode pellets were dried at 150 °C for 24 hours, followed by cooling at room temperature, before the porosity test was conducted.

3. Results and Discussion

3.1 Morphology of LSCF-SDCC-Ag Composite Cathode Powders

The images of the microstructures of LSCF–SDCC and the LSCF–SDCC–Ag composite cathode powder were captured using a FESEM micrograph (Figures 1(a) to 1(e)). The FESEM micrograph showed that the particles tended to agglomerate as Ag content increased. As observed, the particle size was in nanoscale. The particle size of the composite cathode powder LSCF–SDCC produced via HEBM was less than 200 nm. The HEBM has also been proven to produce a composite cathode powder measuring below 200 nm [13]. A composite cathode powder with a small size (between 100–200 nm) was desirable because of the reduced particle size and increased surface area. This phenomenon enlarged the TPB area for oxygen reduction reaction to occur in the cathode, which might directly improve the cathode performance [14].

The average particle size was taken from five different spots of the FESEM images with 100 measurements for each sample. Table 1 lists the average particle sizes of LSCF–SDCC without Ag and LSCF–SDCC–Ag with Ag content ranging from 1–5 wt%. The average particle size ranged from 80.0–89.2 nm. The composite cathode of LSCF–SDCC without Ag had the lowest average particle size (80.0 nm), whereas the composite cathode LSF–SDCC with a 5% addition of Ag content had the highest average particle size (89.2 nm). The particle size tended to increase as the amount of added Ag was increased. The average particle size of the composite cathode powder did not change drastically with the amount of Ag content (1–5 wt%). As the average particle sizes ranged from 80–89.2 nm, all of the composite cathode powders met the required characteristics and were thus suitable for composite cathode powder materials [15–16]. This conclusion is based on the criterion that particle sizes below 1 µm can provide an appropriate surface area absorption in the ceramic body. Hence, the average particle size of all composite cathode powder of LSCF–SDCC–Ag (1–5 wt%) in the present study satisfied the requirement of particle size for a SOFC’s cathode powder. The nano-particles powder with large surface areas will extend the TPB and supply an increased catalytic activity toward the oxygen reduction reaction (ORR), consequently improving electrochemical performance [17].
Figure 1. FESEM micrographs of composite cathode LSCF–SDCC (a) without Ag, (b) Ag 1 wt.%, (c) Ag 2 wt.%, (d) Ag 3 wt.%, (e) Ag 4 wt.%, and (f) Ag 5 wt.% at 50K magnification.

Figure 2. Measurement of average particle size from FESEM image of LSCF–SDCC–Ag composite cathode powder.
Table 1. Average particle size of composite cathode powders LSCF–SDCC–Ag based on different amounts of added Ag

| LSCF–SDCC–Ag (wt%) | Particle size (nm) |
|--------------------|--------------------|
| 0                  | 80.0 ± 17.4        |
| 1                  | 81.5 ± 12.4        |
| 2                  | 83.7 ± 14.0        |
| 3                  | 86.8 ± 14.7        |
| 4                  | 87.8 ± 15.3        |
| 5                  | 89.2 ± 16.4        |

3.2 Porosity of LSCF-SDCC Composite Cathode Pellets

The porosity values of the cathode pellets for different sintering temperatures and various amounts of Ag content are shown in Figure 3 below. The increasing amount of Ag clearly decreased the porosity of the LSCF–SDCC–Ag composite cathode pellets. The particle size of LSCF–SDCC–Ag also dramatically affected the porosity value of the composite cathode pellet, such that the increased size of the particle with Ag content significantly reduced the porosity. Nevertheless, high sintering temperatures produced dense bodies, which affected the porosity of the LSCF–SDCC–Ag [8, 18].

Researchers believe that the LTSOFC achieves optimal ionic conductivity when porosity is approximately 30%. Several researchers suggested that the porosity of the cathode should range from 20% to 40%. Cathode components should have acceptable porosity to allow for a sufficient amount of oxygen to flow through the cathode, reaching the cathode–electrolyte region for ORR to occur. Optimal cathode porosity also produces the best power output from the LTSOFC [19]. Therefore, the implementation of a sintering temperature higher than 600 °C for LSCF–SDCC–Ag was avoided to ensure that the value of porosity would not be lower than 20%.

![Figure 3. Average porosity of sintered pellet LSCF-SDCC-Ag at 500, 550 and 600°C](attachment:Figure_3.png)
4. Conclusions
The present work investigated the effect of Ag as an additive element on a composite cathode, LSCF–SDCC–Ag (mixed using the HEBM). The morphological and physical characteristics of the composite were examined in relation to the 50% weight fraction of the SDCC electrolyte. The FESEM micrographs indicated that adding Ag to the composite cathode powder made the powder homogeneous and produced particle sizes ranging from 100–200 nm. The particle sizes of LSCF–SDCC–Ag increased with the increase of the Ag content. The porosity value decreased as the Ag content and sintering temperature increased. However, the porosity percentage was within the acceptable range of 26.6% to 33.8%. Finally, the influence of the addition of Ag on the morphological and physical properties of LSCF–SDCC composite cathodes was discussed briefly.

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