

Influence of Ag on the Chemical and Thermal Compatibility of LSCF-SDCC for LT-SOFC

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Abstract. In addition to the good electrochemical performance criteria in solid oxide fuel cell (SOFC) applications, cathode material must match thermal expansion with other SOFC components. Thus, effects of Ag on thermal mismatch, chemical reactions, and microstructure are investigated. Ag (1 wt% to 5 wt. %) was mixed with La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF6428) and Sm-doped ceria carbonate (SDCC) composite cathode powder. LSCF6428-SDCC-Ag samples were sintered at 600 °C for 2 h. The thermal expansion coefficients (TECs), which were determined using a dilatometer, indicated relatively less TEC mismatch between LSCF-SDCC-Ag cathodes composite and SDCC electrolyte. The average TEC value obtained from 20 °C to 600 °C implied that LSCF-SDCC-A5 (5 wt. % Ag) showed better thermal matching ($13.18 \times 10^{-6} \text{ K}^{-1}$) with SDCC electrolyte ($12.84 \times 10^{-6} \text{ K}^{-1}$) and achieved better compatibility. The X-ray diffraction patterns indicated that the LSCF6428-SDCC-Ag peak increased with the increase in the amount of Ag. Scanning electron microscopy analysis showed that Ag was capable of maintaining the porosity that is required for cathodes (20%–40%). Results showed that Ag exhibited desirable thermal and chemical compatibility with LSCF-SDCC. Thus, LSCF6428-SDCC-Ag can be used as a composite cathode for low-temperature SOFCs.

Introduction

Fuel cells allow the direct conversion of chemically stored energy into electrical energy by means of electrochemical oxidation of various fuels. Solid oxide fuel cells (SOFCs) are considered to be among the most promising fuel cells and have been investigated in energy conversion devices with high efficiency, low pollution emission, and extensive fuel flexibility. In SOFCs, an oxygen reduction reaction occurs at the cathode to produce oxygen anions, which then move through a dense oxygen ion-conducting electrolyte to the anode [1]. The cathodes for low-temperature (LT)-SOFCs should possess high electrical and ionic conductivities, enhanced electrode reaction activity, long-term stability, and adequate porosity for gas transport [2]. In SOFC applications, a satisfactory cathode material must meet other requirements such as a thermal expansion match with other components [3]. Thermal expansion coefficient (TEC) is one of the most important factors that ensure reliability of a SOFC system [4].

All of the SOFC components are solid and thus, mismatches in TECs between materials can become a serious problem during fabrication or at thermal cycles during operation. A difference in TEC between a cathode and an electrolyte at $7 \times 10^{-6} \text{ K}^{-1}$ can result in a 10% chance of delamination occurring at the first 500 h of operational [4]. Therefore, the TEC of perovskite has to be considered and should be matched with the electrolyte to avoid a high mismatch with the electrolyte. An excessively high stress can lead to possible delamination at the interface [5]. The trend of TEC value demonstrates that increased electrolyte amounts in the composite cathode bring the TEC of

the cathode closer to that of the electrolyte [6]. A TEC difference of less than 10% [6] between the cathode and the electrolyte is suitable for mechanical compatibility to prevent delamination during processing or applications at elevated temperatures. Thus, developing cathode materials with high electrocatalytic activity is necessary to ensure oxygen reduction reaction and high oxygen ion conductivity for oxygen transport through the composite cathode at LTs; such cathode materials should also exhibit less thermal compatibility mismatch. Ag, which has excellent catalytic activity for oxygen reduction, is applied in LSCF6428-SDC with $14.4 \times 10^{-6} \text{ K}^{-1}$ TEC value [7] to develop an operable LT-SOFC [8]. The use of Ag in composite cathode has been reported by various researchers [8–10]. Ag is also a potential candidate because of its relatively low cost, high electrical conductivity, capability of reducing surface resistance and improving the efficiency of current collection from the cathode, and its ability to realize the LT sintering process [8]. The melting point of Ag is 961.78 °C [2], which limits the operating temperature of SOFCs. However, Ag operates at LT and is widely used as electrodes for various electrochemical devices; Ag has been used in a SOFC [2]. In the present study, the TEC match and chemical reaction characteristics of the composite cathode LSCF6428-SDCC-Ag are studied with varied amounts of Ag.

Experimental Procedure. First, 1, 3, and 5 wt.% Ag (Sigma-Aldrich, Malaysia) was mixed with composite LSCF-SDCC cathode powders. A mixture of 80 wt.% SDC nanopowder (Sigma-Aldrich, Malaysia) with 20 wt.% carbonates (67 mol.% Li_2CO_3 :33 mol.% Na_2CO_3) was prepared through conventional solid-state reaction. Subsequently, 50 wt.% SDCC electrolyte powder was mixed with 50 wt.% perovskites LSCF6428 (Kceracell, Taiwan) powder. Using low energy milling speed, the Ag was dry milled together with LSCF-SDCC using a milling machine (Fritsch Pulverisette 6, Germany). The LSCF-SDCC-Ag composite powders were then ground in an agate mortar and calcined at 750 °C for 2 h with a heating rate of 5 °C min^{-1} to obtain the desired composite cathode powder. The composition based on Ag amount is shown in Table 1. Uniaxial press method was used to prepare cylindrical samples (20 mm long and 6 mm in diameter) of LSCF-SDCC-Ag composite cathode for TEC analysis. The samples were then sintered at 600 °C for 2 h.

Table 1. Composition of composite cathode with varied amounts of Ag

Samples	Ag [wt.%]
LSCF-SDCC	-
LSCF-SDCC-A1	1
LSCF-SDCC-A3	3
LSCF-SDCC-A5	5

Characterization Method. X-ray diffraction (XRD, Bruker D8 Advance) was used to identify the chemical compatibility of LSCF6428-SDCC-Ag cell using Cu Ka radiation ($\lambda = 0.15406 \text{ nm}$) at room temperature. The diffraction patterns were collected by step scanning at 0.02° in the 2θ range of 20° to 80° . The relative TEC was measured in air from room temperature to 600 °C at 5 °C min^{-1} . The TECs of the samples were measured using a horizontal push rod dilatometer (Netzsch DIL 402C) with an Al_2O_3 reference. The surface morphology and homogeneity of the cathode composite were observed via scanning electron microscopy (SEM, Zeiss Evo MA, UK). Porosity and density were evaluated using the Archimedes principle.

Results and Discussion. Chemical compatibility for various concentrations of Ag on sintered LSCF-SDCC-Ag samples was examined via XRD test with 03-065-2871 as reference pattern (Fig. 1). The XRD patterns illustrate that the increase in peak intensities was due to the increase in Ag concentration. The XRD results showed that Ag formed a cubic structure. The introduction of Ag into the composite LSCF6428-SDCC cathode did not affect its composite cathode structure because no secondary peaks appeared after the powder preparation process [9]. The absence of secondary

peaks means that the components in the composite cathode yielded better results with their own function and advantages.

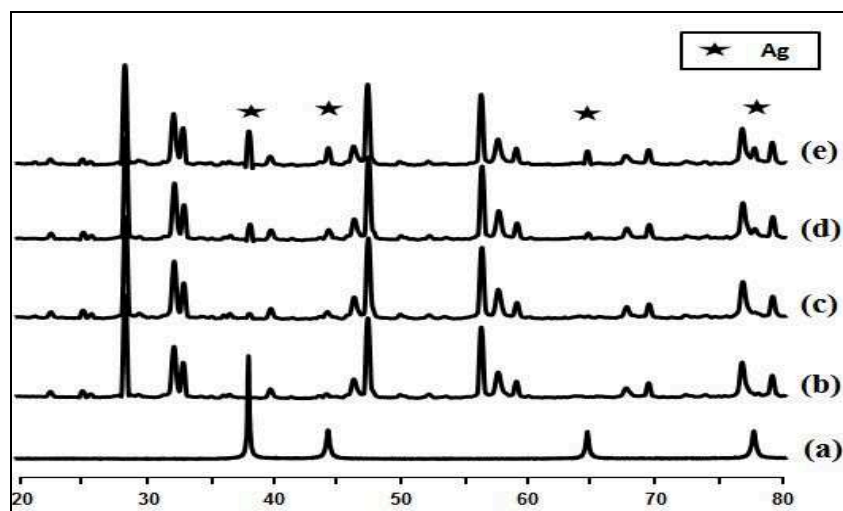


Fig. 1. XRD patterns of purity composite cathode: (a) Ag; (b) LSCF-SDCC; (c) LSCF-SDCC-A1; (d) LSCF-SDCC-A3; and (e) LSCF-SDCC-A5.

The porosity and density results indicate that the addition of Ag increased the bulk density and decreased the porosity of LSCF-SDCC-Ag composite cathode. The porosity of the composite cathode without Ag was 32.80%; however, the addition of 5 wt.% Ag reduced the porosity to 27.95%. The density of the cathode was 3.79 g cm^{-3} without Ag and 4.08 g cm^{-3} with 5 wt. % Ag (Fig. 2). Incorporating Ag in the ceramic phase can prevent Ag from sintering, thereby retaining the porosity that is required for a cathode electrode [10]. Retaining the required porosity means that sufficient pores (20%–40%) are available for transporting oxidants to the electrochemical reaction sites in the cathode [11]. Su *et al.* [12] demonstrated that incorporating Ag into the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ significantly improves electrocatalytic oxygen reduction performance, enhances current collecting ability, and reduces the electrode ohmic resistance of the cathode.

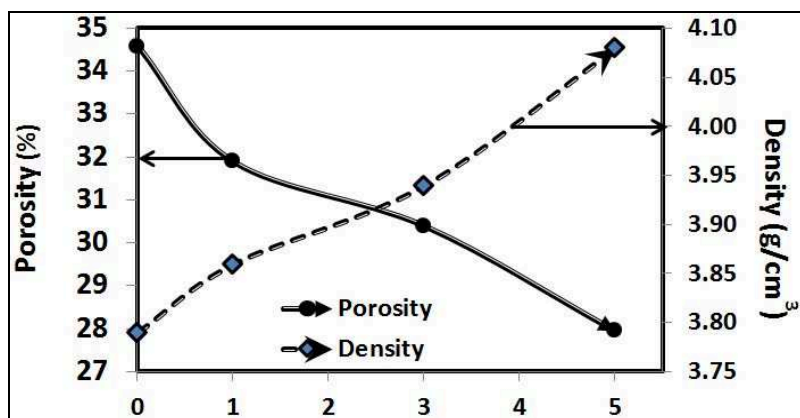


Fig. 2. Porosity and density results for composite cathodes with different Ag concentrations.

Figure 3 shows the SEM micrographs of the composite LSCF-SDCC cathodes (sintered at 600°C for 2 h) with 1 wt.% to 5 wt.% Ag. A back-scattered electron detector was used to obtain the SEM images of the composite LSCF6428-SDCC-Ag cathode. Black spots represent pores on the composite LSCF-SDCC-Ag cathode. The observed surface morphology indicated that the addition of Ag decreased the porosity from 31.90% to 27.95 % for the cathodes with 1 wt.% to 5 wt. % Ag, respectively. The observed internal morphology indicated that the composite cathode became dense after the addition of Ag. These results are consistent with porosity and density results.

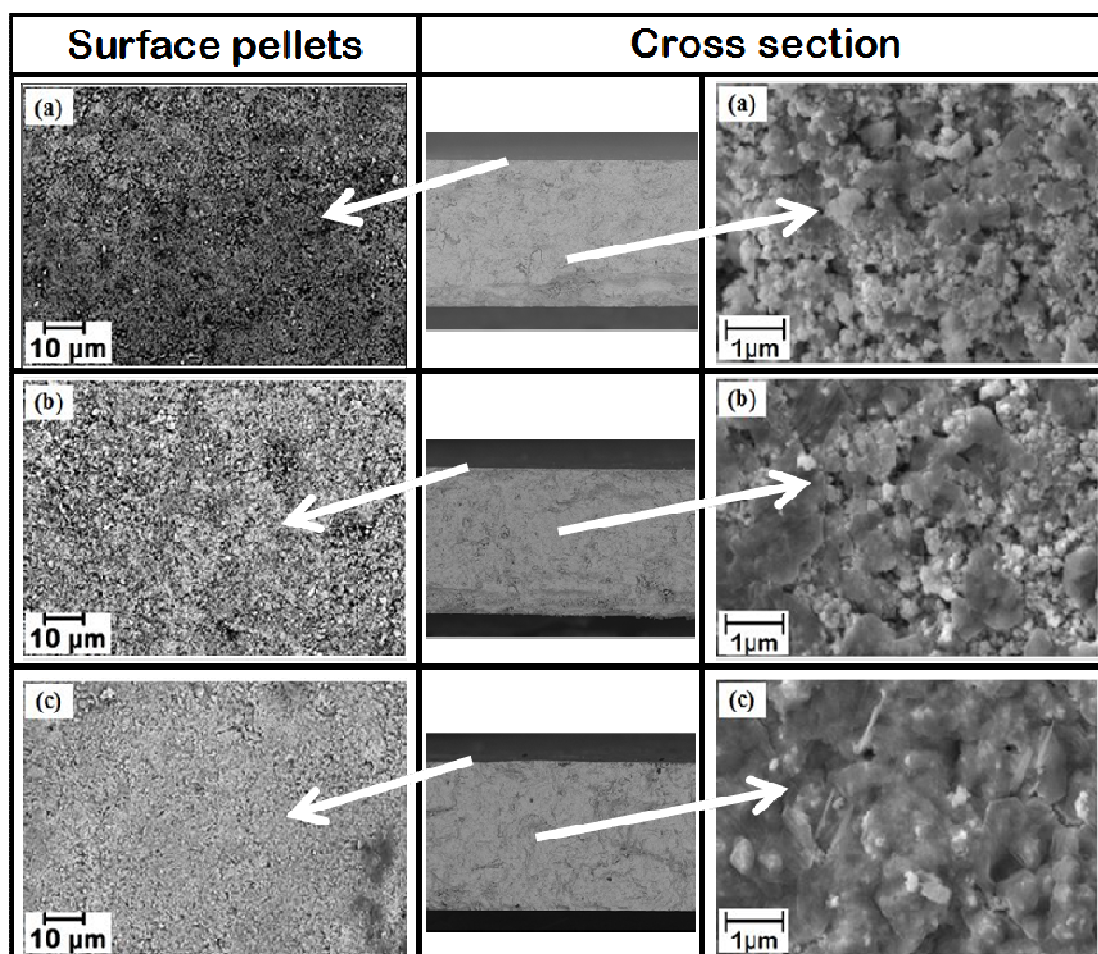


Fig. 3. Morphology of the composite LSCF-SDCC-Ag cathodes (sintered at 600 °C for 2 h) with (a) 1 wt% Ag, (b) 3 wt.% Ag, and (c) 5 wt.% Ag.

The TEC of composite LSCF-SDCC-Ag cathode in the temperature range of 20 °C to 600 °C is shown at Table 2, with a composite electrolyte SDCC as a reference. Tietz [5] found that large differences in TEC may induce large internal stress during the actual application, thereby affecting the operational stability of SOFCs. Therefore, preparing a composite cathode with below $7 \times 10^{-6} \text{ K}^{-1}$ [4] and 10% different [6] to avoid delamination [4]. In the present study, the TEC values decreased with the increase in Ag concentration. The addition of 5 wt.% Ag in LSCF-SDCC gives the lowest TEC mismatch with the SDCC electrolyte at the percentage difference of 2.65% ($0.34 \times 10^{-6} \text{ K}^{-1}$) compared to the LSCF-SDCC with 3 wt.% Ag, 1 wt.% Ag and without Ag which yielded a mismatch of 4.36%, 5.14%, and 4.21% respectively. Therefore, in this temperature range and based on this criterion, the LSCF-SDCC-A5 shows the most appropriate matches and potential to improve the performance of LT-SOFC [4].

Table 2. TECs of SDCC electrolyte with LSCF-SDCC-Ag cathode.

Sample	Average TEC ($^{\circ}\text{C}/\text{K}$) (20–600 °C)
SDCC	12.84
LSCF-SDCC	13.38
LSCF-SDCC-A1	13.50
LSCF-SDCC-A3	13.40
LSCF-SDCC-A5	13.18

Conclusions

Ag exhibited good thermal compatibility with the composite LSCF-SDCC cathode after sintering at 600 °C for 2 h. Thus, 1 wt.% to 5 wt.% of Ag was appropriate for incorporation with LSCF-SDC composite cathode. Ag plays an important role in improving chemical reactions when the cathodes are used as fine conductors, as well as in decreasing TEC mismatch. The results of this study show that Ag can be used as a metallic catalyst in LSCF-SDCC cathodes for LT-SOFCs.

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