Optimisation of screen-printed La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathode film for intermediate temperature proton-conducting solid oxide fuel cell application

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Abstract. The effect of thin film properties on the electrochemical performance of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) cathode was investigated. A single phase of sol-gel derived LSC cathode powder is produced using ethylene glycol (EG) and activated carbon (AC), pressed into a pellet and turned into an LSC cathode slurry. The slurry is screen printed with different printing numbers (2, 4, 6 and 8 times) on the BaCe$_{0.54}$Zr$_{0.36}$Y$_{0.1}$O$_3$ (BCZY) electrolyte substrate to fabricate LSC|BCZY|LSC symmetrical cell. The EG-based LSC cathode recorded the lowest area specific resistance (ASR) value ($0.11 \text{ \Omega \ cm}^2$) in the symmetrical cell fabricated with printing number of 2 times (film thickness = $3.90 \pm 0.18 \text{ \mu m}$, film porosity = $23.09 \pm 0.42 \%$). The AC-based LSC cathode requires a high printing number of 6 times (film thickness = $6.76 \pm 0.50 \text{ \mu m}$, film porosity = $21.98 \pm 0.52 \%$) to obtain the lowest ASR value ($0.15 \text{ \Omega \ cm}^2$) because the electrical conductivity of the AC-based LSC cathode is lower than that of the EG-based LSC cathode. Overall, this work shows that the variations in the ASR values of the same LSC materials prepared with different chemical additives are affected by the properties of the printed thin film.

1. Introduction

Fuel cell such as solid oxide fuel cells (SOFCs) are an electrochemical device that converts the chemical energy of the supplied fuel and oxidant directly into electricity via electrochemical processes. SOFC made of proton-conducting electrolytes (H$^+$–SOFC) has gained greater attention than conventional SOFC made of oxygen ion-conducting electrolytes (O$^2$–SOFC) for application at intermediate temperatures (IT, 500 °C – 800 °C). However, SOFCs operate at IT encounter challenges in terms of high cathode polarisation resistance ($R_p$) due to low electrocatalytic activity of cathode materials for oxygen reduction reaction (ORR) [1]. As such, cathode materials, which possess high catalytic activity, must be developed for IT H$^+$–SOFC. Cobalt (Co)-containing mixed ionic–electronic
conducting (MIEC) perovskite oxides have been the hotspot of research on SOFC cathodes due to their high electronic and oxide ion conductivity [1,2]. One of Co-containing MIEC perovskite oxides is lanthanum strontium cobaltite (La0.6Sr0.4CoO3-d, LSC).

LSC is frequently employed as a cathode material for application of O2–SOFC containing gadolinium-doped ceria (Ce0.9Gd0.1) electrolytes [2–7]. To date, to the best of the authors’ knowledge, only one study has reported the use of LSC material in H2–SOFC containing yttrium and ytterbium-doped barium cerate-zirconate (BaCe0.9Zr0.1Y2O3-d) electrolyte [8]. The potential of LSC as cathode material for IT H2–SOFC must be further evaluated. In addition, few studies have investigated on the optimisation of LSC cathode film properties, particularly for the same LSC materials produced by sol-gel method and added with different chemical additives. Therefore, this work aimed to evaluate the screen-printed thin film properties (thickness and porosity) effect on the electrochemical performance of LSC cathode prepared by sol-gel method with ethylene glycol (EG) as polymerising agent and activated carbon (AC) as dispersant.

2. Materials and methods

2.1. Preparation of sample

LSC cathode powder was prepared through sol-gel method with citrate-EDTA as described elsewhere [9,10]. La(NO3)3·6H2O, Sr(NO3)2 and Co(NO3)2·6H2O were used as precursor materials. Chemical additives, namely EG and AC, were employed as polymerising agent and dispersing agent/dispersant, respectively. A stoichiometric amount of the precursor materials mixture was first dissolved in deionised water, and added with a stoichiometric amount of citric acid and EDTA. The pH of the mixture was adjusted to 0.5. The mixture was then added with chemical additive (EG or AC) and slowly heated at 100 °C – 150 °C and 150 °C – 250 °C to evaporate the water and dry the obtained viscous gel. The as-synthesised powder was calcined at 900 °C for 5 h. The calcined powder synthesised using EG and AC was labelled as EG900 and AC900, respectively. A cathode pellet was prepared by pressing the calcined powder in a 13 mm mould by using a hydraulic press machine under isostatic pressure of ~ 370 MPa (5 tons) for 1 min. The pressed pellet was sintered at 1200 °C for 2 h to obtain a dense pellet. A symmetrical cell of LSC|BaCe0.5Zr0.3Y0.1O3 (BCZY) [LSC] was prepared by screen printing the LSC cathode slurry onto the surfaces of BCZY electrolyte pellet with different printing numbers (2, 4, 6 and 8 times), followed by sintering process at 900 °C for 2 h. The details for the preparation of pellets and symmetrical cells preparation were described elsewhere [9].

2.2 Characterisation of sample

An X-ray diffractometer (XRD, D8-Advance, Bruker, Germany) was used to evaluate the phase formation in the calcined EG900 and AC900 powders within the 2θ of 20° to 80°. The calcined powders microstructure images were captured using a scanning electron microscope (SEM, Zeiss, Germany). Image processing software (ImageJ) was used to determine the mean particle size (D50) in the SEM micrograph. Archimedes’ method was used to determine the density of the sintered cathode pellet [11]. The surface and cross-section microstructure images of the cathode pellet and symmetrical cell were captured using Hitachi U1510 SEM (Japan). The captured images were used to measure the porosity (by adjusting the threshold) and thickness of the cathode film by using ImageJ software. The electrical conductivity (σ) of the sintered cathode pellet was measured through van der Pauw method using a Keithley 2400 combined current source (I = 100 mA) and voltmeter at 500 °C to 800 °C in the presence of air flow (100 mL min-1). The details for the σ measurement of the cathode pellet were described elsewhere [9]. The electrochemical impedance characteristics of the fabricated symmetrical were determined in potentiostatic mode by using a ZIVE SP2 electrochemical workstation (ZIVE LAB WonATech, Korea) at open circuit voltage (OCV) under a sinusoidal voltage of 5 mV. The electrochemical impedance characteristics were measured over the frequency range of 100 mHz to 1 MHz at 500 °C to 800 °C in air at 100 mL min-1. The electrochemical impedance data were analysed by using ZMAN™ 2.2 β software (ZIVE LAB). The impedance diagram were plotted in real impedance (Zreal or Zr) versus imaginary impedance (Zim or Z′). Area specific resistance (ASR) value was calculated using the following equation: \[ \text{ASR} = \frac{R_p \times A}{2}, \] where \( R_p \) refers to the polarisation.
resistance at the interfacial layer of cathode-electrolyte, and $A$ refers to the specific active area of the cathode (0.50 cm$^2$).

3. Results and discussion

3.1. Phase formation and microstructure of the synthesised powder

The XRD patterns and typical morphology images of the calcined EG900 and AC900 powders are shown in Figure 1. The formation of a single perovskite phase of LSC in the calcined EG900 and AC900 powders was confirmed by the XRD measurement. All the peaks in the XRD patterns matched with the ICDD reference code 00-048-0121 (structure: cubic; space group: Pm-3m) and can be indexed to their Miller indices (hkl) of (100), (110), (111), (200), (210), (220), (300) and (310). Both powders samples consist of homogeneous and regular-shaped of particles that are connected to one another. The $D_{SEM}$ of EG900 and AC900 powders are 0.26 ± 0.06 μm and 0.22 ± 0.05 μm, respectively.

![XRD patterns and SEM micrograph images of EG900 and AC900 powders](image)

*Figure 1. XRD patterns and SEM micrograph images of EG900 and AC900 powders*

3.2. Microstructure and electrical conductivity of the fabricated pellets

The LSC cathode pellets of EG900 and AC900 powders are highly dense with relative density ($\rho_{rd}$) values of 96.56 ± 0.90 % and 95.15 ± 0.53 %, respectively after sintering at 1200 °C. The formation of grain and grain boundaries without pores is clearly shown in the SEM images on the surfaces of dense LSC cathode pellets (Figure 3). Figure 4 shows the graph of electrical conductivity ($\sigma$) versus temperature ($T$) of the dense LSC cathode pellets. The $\sigma$ values of both LSC cathode pellets decreased with increasing temperature from 500 °C to 800 °C, indicating a metallic-like behaviour, similar to other reports for the same material [2,12,13]. This observation is due to the transition of energy configuration from the low-to-high-spin state, leading to electron transition from localised to itinerant in trivalent cobalt ions (Co$^{3+}$). The transition is also due to an increase in the number of oxygen vacancies, resulting in breaking of Co-O-Co bonds, and decreased $\sigma$ [14]. The LSC cathode pellet of EG900 powder has higher $\sigma$ than that of AC900 powder because of the slightly higher $\rho_{rd}$ value of the EG900 cathode pellet than the AC900 cathode pellet. For bulk $\sigma$ measurement, a dense pellet is specifically required because the measurement greatly depends on microstructure and pore volume fraction properties. A pellet with high density and low porosity enlarges the effective contact area amongst grains and ensures the continuity of the electric path, leading to a high $\sigma$ value by reducing internal blocking [9,15].
3.3. **Microstructure and electrochemical characteristics of the fabricated symmetrical cells**

Figure 3 represents an example of the SEM image at cross-section and on the cathode film surface of EG900-based LSC|BCZY|LSC symmetrical cell fabricated with printing number of 2 times. The cathode particles were homogeneously distributed and had sufficient porous structure.

**Figure 3.** SEM images at (a) cross-section and (b) cathode film surface (red colour indicates pores) of EG900-based symmetrical cells fabricated with printing number of 2 times

Figure 4 shows the electrochemical impedance spectrum of EG900- and AC900-based symmetrical cells with different cathode film printing numbers. Impedance arcs were analysed using an electrical equivalent circuit as shown in Figure 4(c). The measured and calculated values of thickness, porosity and ASR at 800 °C for each symmetrical cell with different cathode film printing numbers are tabulated in Table 2. An increase in the film printing number resulted in an increase in the film thickness and a decrease in the film porosity. These results are due to the increase in the numbers of cathode particles deposited in the cathode film as the film printing numbers increased. For the EG900-based symmetrical cell, the lowest ASR value of 0.11 Ω cm² was recorded at the lowest printing number of 2 times (2x), leading to the optimum thickness (3.90 ± 0.18 μm) and porosity (23.09 ± 0.42 %) of the film for the cathode electrochemical reaction, namely oxygen.
dissociation/adsorption and mass transfer of oxide ion (O\textsuperscript{2-}). Conversely, the AC900-based symmetrical cell recorded the lowest ASR value of 0.15 Ω cm\textsuperscript{2} at the printing number of 6 times (6x). The AC900-based cathode film with printing number of 2 times (2x) might be extremely thin. Thin films exhibit poor cathode electrochemical reaction activity on the surface and at the cathode-electrolyte interface due to few active sites [16]. Thus, adding active cathode particles by increasing the printing number (from 2 to 4 times) is required to accelerate the cathode electrochemical reaction in the AC900 cathode film. However, this approach is only valid up to a certain thickness limit (6 times, 6x) that depends on the cathode microstructure. Beyond this limit, the ASR value increases, and the cathode behaves as a semi-infinite electrode [16,17]. The obtained results are in agreement with the σ measurement data. The AC900-based cathode film requires thicker cathode film layer (more active cathode particle) than the EG900-based cathode film to provide the lowest ASR value given that the σ value of the AC900-based LSC cathode is lower than that of the EG900-based LSC cathode.

Figure 4. Impedance spectrum of (a) EG900-based and (b) AC900-based symmetrical cells with different numbers of film printing at 800 °C and (c) adopted electrical equivalent circuit to analyse the impedance data

Table 1. Values of film thickness, surface porosity and ASR of symmetrical cells prepared using EG900 and AC900 powders with different numbers of film printing

| Symmetrical cell | Number of printing | Film thickness (μm) | Film surface porosity (%) | ASR at 800 °C (Ω cm\textsuperscript{2}) |
|------------------|--------------------|---------------------|--------------------------|---------------------------------|
| EG900            | 2x                 | 3.90 ± 0.18         | 23.09 ± 0.42             | 0.11                            |
|                  | 4x                 | 4.36 ± 0.30         | 22.50 ± 0.40             | 0.68                            |
|                  | 6x                 | 5.42 ± 0.33         | 22.08 ± 0.32             | 0.39                            |
|                  | 8x                 | 5.88 ± 0.40         | 21.17 ± 0.37             | 0.47                            |
| AC900            | 2x                 | 4.86 ± 0.57         | 24.23 ± 0.30             | 0.88                            |
|                  | 4x                 | 5.68 ± 0.48         | 23.21 ± 0.49             | 0.75                            |
|                  | 6x                 | 6.76 ± 0.50         | 21.98 ± 0.52             | 0.15                            |
|                  | 8x                 | 7.68 ± 0.60         | 20.53 ± 0.29             | 1.10                            |
4. Conclusions
A single perovskite phase of LSC cathode powder was successfully prepared through sol-gel method with EG and AC as polymerising agent and dispersant, respectively. The highly dense sintered EG900-based and AC900-based LSC cathode pellets possess $\sigma$ values of 1594 S cm$^{-1}$ and 1244 S cm$^{-1}$, respectively at 800 °C. The LSC cathode film was fabricated on BCZY electrolyte through screen printing technique with different printing numbers. The properties of the printed film, namely thickness and porosity were essential in determining the ASR of the same LSC cathode prepared with different chemical additives. The fabricated symmetrical cell under the optimum number of printing resulted in the lowest ASR value. LSC materials with lower $\sigma$ value require thicker cathode film than those with higher $\sigma$ value to increase the numbers of the active cathode particles for improved cathode electrochemical reaction activity. EG900-based (0.11 $\Omega$ cm$^{-2}$) and AC-based (0.15 $\Omega$ cm$^{-2}$) LSC materials exhibited ASR values lower than 1.00 $\Omega$ cm$^{-2}$ at IT of 800 °C. Hence, the fabricated LSC materials could be used as cathodes for H$^+$–SOFC containing BCZY electrolyte.

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