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Influence of layer numbers on the structural and electrical performance of cobalt-free $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode for intermediate-temperature solid oxide fuel cell application

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Abstract. The influence of layer numbers on the structural and electrical performance of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cobalt-free cathode was studied. The $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode films fabricated using screen-printing technique with different layer numbers sintered at 1300 ℃ for 2 h were characterised using field-emission scanning electron microscopy (FESEM) for structural analysis and four-point van der Pauw method for direct current electrical conductivity (σ_{DC}). FESEM micrographs confirmed that the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cobalt-free cathode films (fabricated with different layer numbers) adhered well on the samarium doped ceria electrolyte surface. The porous films were also uniform without crack formation. The thicknesses of the as-fabricated cathode films were 9.0 ± 0.5, 25.6 ± 1.0, 54 ± 0.6, 71.2 ± 1.4 and 92.2 ± 1.6 μm for layer numbers 1 (1×), 4, 7, 10 and 13 times (13×), respectively. The electrical performance of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cobalt-free cathodes was reported within the operating temperature ranging from 550 ℃ to 800 ℃ as the targeted application was the intermediate temperature solid oxide fuel cell. The layer numbers (thickness) dependence of σ_{DC} suggested a mechanism of long electron pathway at the surface and through the films due to the increase in pores. While the sintering temperature is kept constant, increasing in the number of layers increased the pores accordingly. Hence, the lowest σ_{DC} value at 800 ℃ (2.45 S cm^{-1}) is obtained for $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode films with high number of layers (13×). The highest σ_{DC} value (16.46 S cm^{-1}) was recorded for a single layer (1×) $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode film. Although the conductivity value was still far from the desired theoretical conductivity of 100 S cm^{-1}, this result was better than that of the literature that reported the same composition, thereby showing that the quality of cathode film was improved.

1. Introduction

Fuel cell is an energy converter device that produced electricity through the electrochemical reaction between fuels (oxygen and hydrogen) [1,2]. Fuel cell has several types, and each of which can be

differentiated by its electrolyte materials [3]. Fuel cell that was built from the ceramic-based electrolyte is called solid oxide fuel cell (SOFC). The utilisation of ceramic materials allows SOFC to operate at high temperature which results in excellent efficiency. Traditional SOFC that used in power plant, such as in combined heat power system, normally can reach until 1000 ℃. To allow the variation of SOFC applications, researchers mainly aimed to lower the operational temperature [4,5]. The reduction of the operating temperature not only expands the applications for this type of fuel cell but also resolves some issue related to cell degradation and durability [6]. However, the reduction of the temperature required development of new materials at each component of the SOFC as the commonly used material, such as yttria-stabilised zirconia (YSZ, electrolyte), lanthanum strontium manganite (cathode) and NiO – YSZ (anode), shows poor performance in the region with low operation temperature [7].

For cathode, the latest approach is the use of cobalt-free mixed ionic-electronic conductor based materials [8,9]. Cobalt removal is crucial to reduce the thermal mismatch between cathode and electrolyte, thereby avoiding delamination to occur [10]. When delamination occurs, the overall performance of the SOFC will decrease drastically as the electronic and ionic pathways were disconnected. In the past 10 years, researchers have witnessed the synthesis process of numerous novel perovskite-based cobalt-free cathode materials by using a doping approach. For cobalt-free $SrFeO_{3-\delta}$-based materials, Ti shows good performance in stabilising the cubic structure [11]. Various works related to the ionic (electrochemical) side of the cobalt-free Ti-doped $SrFeO_{3-\delta}$ has been conducted to prove the potential of this material in operational temperature 800 ℃ [12–14]. For the electronic part, the direct current conductivity (σ_{DC}) has been extensively studied by observing the doping behaviour [12,13,15]. Meanwhile, the structural parameter together with electrode thickness determines the mechanism underlying the transport of the electron through the electrode [16]. Unfortunately, the effects of the structural parameter and cathode thickness for Ti-doped $SrFeO_{3-\delta}$ (represented as $SrFe_{1-x}Ti_xO_{3-\delta}$) remains unexplored. Thus, this work aimed to study the effect of cathode thickness (in a function of layer number) on the structural and electrical performances, specifically on the σ_{DC} of cobalt-free $Sr_{0.5}Fe_{0.5}Ti_{0.5}O_{3-\delta}$ (x = 0.5) cathode.

2. Methods

2.1. $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ Cathode Powder Preparation

The precursor cathode powders were prepared using a combustion method. A stoichiometric amount of fuel (glycine) was added into the mixture of nitrate solutions ($Sr(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ and $TiO(NO_3)_2$) and stirred for 45 h to obtain homogenous precursor solution using magnetic stirrer. All materials were purchased from Sigma-Aldrich. Next, the drying process at a temperature of 150 ℃ (1.5 h) was conducted using a hot plate to eliminate excess water. The combustion was started by increasing the hotplate temperature to 350 ℃ which produced black ash called as precursor powders. Then, calcination at 1300 ℃ (5 h) was performed to yield the desired $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode powders. The purity of as-synthesised cathode powders was proved using X-ray diffraction (XRD) analysis. Findings for primary and refined XRD patterns were reported in previous works [17,18].

2.2. Fabrication $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ Cathode Ink Formation and Half-Cell Fabrication

The as-synthesised $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders underwent high energy ball milling (FRITSCH PULVERISETTE 6, Germany) together with acetone (250 rpm for 2 h). Then, the mixture was dried at 90 ℃ (12 h). Afterward, the dried cathode powders with the volume percentage 26 % [19] were mixed together with a dispersant (hypermer KD15), solvent (terpineol) and binder (ethyl cellulose) to form a homogenous cathode ink. The mixing process was conducted using triple-roll miller (EGM-65, ELE, China). Half cells with cathode/electrolyte configuration were produced using screen printing technique. Prior to screen printing, the electrolyte substrate (diameter = 25 mm) made from samarium doped ceria (SDC) (Sigma-Aldrich) were prepared via pressing method (CARVER, USA) with a compaction pressure of 52 MPa and sintered at a temperature of 1400 ℃ (6 h). Then, a different number of cathode

layers with an area of 1 cm^2 was screen printed on one side of the SDC electrolyte surfaces to form a half cell of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$/SDC. The layer numbers that were considered included 1 (1×), 4 (4×), 7 (7×), 10 (10×) and 13 times (13×). The formation of each layer was followed by a drying process. Upon the completion of desired layer numbers, the symmetrical cells were then sintered at 1300 ℃ (2 h).

2.3. Structural and Electrical Conductivity Characterisation

The morphology of the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ films were characterised via field-emission scanning electron microscopy (FESEM; JEOL JSM-6701F) by using two approaches, namely, surface and cross-sections. For direct current electrical characterisation, the σ_{DC} of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode with different layer numbers was measured using the four-point Van der Pauw technique. The measurement was performed at a temperature of 600 ℃ to 800 ℃ in flowing air (200 ml/min), and the current was kept constant (0.001 A).

3. Results and Discussions

3.1. Structural Characterisation of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ Cathodes

The surface and cross-sectioned micrograph for $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode produced with different layer numbers are shown in Figure 1. The porous structure was observed in all films. The difference in the surface micrograph with the increase in layer numbers was insignificant. For cross-sectioned micrographs, the thickness of cathode films increased as the number of layers increased. Each cross-sectioned view showed the formation of well-adhered and uniform $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode films on the SDC electrolyte substrate.

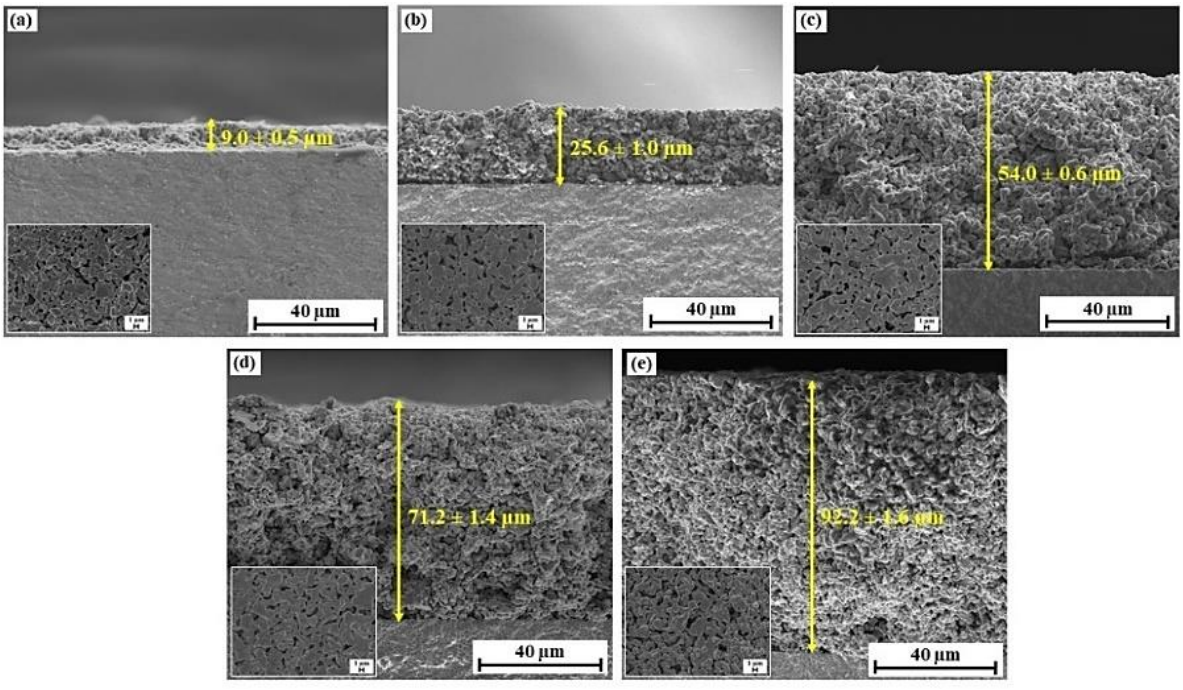

Figure 1. FESEM cross-sectioned and surface micrographs for $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode with layer numbers of (a) 1×, (b) 4×, (c) 7×, (d) 10× and (e) 13×.

The thicknesses of the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode films were 9.0 ± 0.5, 25.6 ± 1.0, 54.0 ± 0.6, 71.2 ± 1.4 and 92.2 ± 1.6 µm for the layer numbers 1×, 4×, 7×, 10× and 13×, respectively. The cross-sectioned micrograph showed that the porosity increased with the increase in either layer number or thickness.

3.2. DC Electrical Conductivity of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ Cathodes

Figure 2 shows the σ_{DC} for $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode films with different layer numbers tested in the temperature ranging from 500 °C to 800 °C. The results showed that all films exhibited semiconducting behaviour, in which the conductivity increased as the operation temperature increased. This result was caused by polaron hopping conduction mechanism that is generally reported in iron-containing cathode materials [20,21]. All cathodes with different layer numbers showed the highest σ_{DC} values at 800 °C, with single-layer cathode (labelled as SP 1×) exhibiting the maximum σ_{DC} value of 16.46 S cm^{-1}. The remaining σ_{DC} values were 8.65, 3.58, 2.53 and 2.45 S cm^{-1} for layer numbers 3×, 7×, 10× and 13× at 800 °C), respectively. All σ_{DC} values obtained for cathode with different layer numbers were still far from the targeted theoretical value (~ 100 S cm^{-1}) to ensure an excellent current collection. However, an improvement was observed when the results were compared to the same composition reported elsewhere [22]. A better σ_{DC} is expected to be obtained in a lower dopant mole ratio (<0.5).

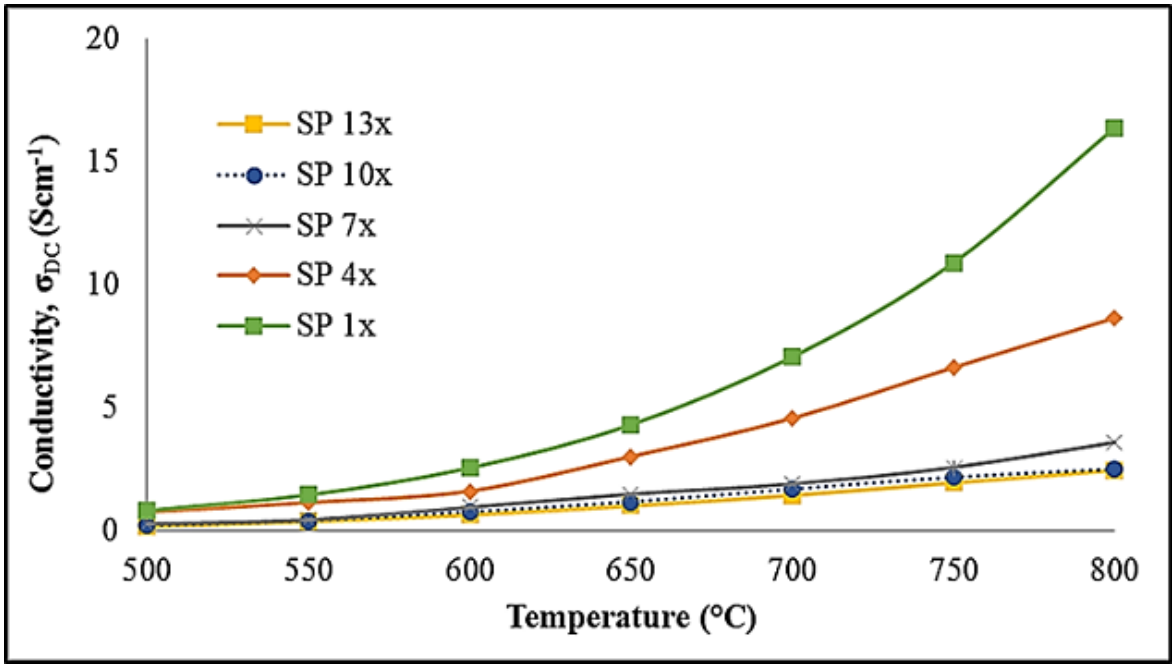

Figure 2. DC electrical conductivity for cobalt-free $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathodes at 500-800 °C.

On the microstructural perspective, as the layer numbers increased, the porosity also increased. An increase in pores resulted in the discontinuity of the electric pathway, thereby decreasing the σ_{DC} values. This result explained the inversely proportional relationship between layer numbers (thickness) and σ_{DC}. Samat el at. (2018) successfully illustrated the effects of porosity on σ_{DC} at the surface and cross-section of the cathode layer [16]. The existence of pores in high volume affects the electron travel distance as the electron attempts to avoid the pores, thereby generating a long pathway through cathode thickness [16].

4. Conclusion

The role of more layer numbers shows a negative effect on the electrical property of cobalt-free cathode $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$, specifically σ_{DC} values. The introduction of a thick layer for cobalt-free $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode generates long electronic pathway, thereby degrading σ_{DC}. The further analysis of the layer number (thickness) optimisation is needed to be evaluated not only by observing the σ_{DC} values but also in terms of the cathode electrochemical performance.

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