INFLUENCE OF SINTERING TEMPERATURE ON THE POLARIZATION RESISTANCE OF $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ – SDC CARBONATE COMPOSITE CATHODE

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The effects of sintering temperature of an LSCF-samarium-doped ceria carbonate (SDCC) cathode composite film on its polarization resistance (Rp) were evaluated in this study. An LSCF-SDCC composite cathode was prepared for cathode film development by electrophoretic deposition (EPD). The LSCF-SDCC composite cathode was prepared at 50:50 weight percentage ratio. An EPD suspension which is based on an organic aqueous solution was used, and a mixture of ethanol and deionized water was used as medium with poly diallyl dimethyl ammonium chloride (PDADMAC) as a dispersing agent. SDCC substrate was used, and EPD was performed on both sides. A symmetrical cell with cathode composite LSCF-SDCC films on both sides of the substrate was subjected to sintering at five different temperatures (from 550°C to 750°C). A symmetrical cell was painted using silver paste before undergoing electrochemical performance test (air condition), in which the impedance, Z data, was measured. The effects of sintering temperature change on element content and film porosity were first investigated by energy-dispersive X-ray spectroscopy, field emission scanning electron microscopy, and J-image analysis. Ceramic-based cathode LSCF-SDCC that was sintered at 600°C exhibited the lowest Rp at a value of 0.68 Ω when operated at 650°C. This study proved that EPD has potential in developing IT-LT solid oxide fuel cell cathode components with high electrochemical performance in terms of Rp values.

INTRODUCTION

Solid oxide fuel cell (SOFC) is an energy conversion device that is highly efficient and ecologically friendly. SOFCs are conventionally used for high-temperature at temperatures around 800 - 1000°C depending on process demands [1]. Studies on this field have resulted in novel ideas, such as reducing the operating temperature of SOFC by introducing new composite materials and nano materials [2]. Reducing the operating temperature into the intermediate zone (500°C to 800°C) lowers energy consumption, material degradation risk, and operational cost of SOFCs [3].

Novel materials have been recently developed to reduce the operating temperature for intermediate-temperature SOFC (ITSOFC) applications, in which all components (anode, electrolyte, and cathode) need to be replaced with materials of higher conductivity at lower temperatures. The scope of this work only involves the cathode component; thus, LSCF is the main material in this study. LSCF has high ionic conductivity at intermediate-temperature operations [4, 5]. This material could potentially reduce the polarization resistance (R_p) and expand the reaction zone of the cathode [6]. To enhance the ionic conductivity of the LSCF-based cathode, electrolyte materials such as samarium-doped ceria carbonate (SDCC) is added to form composite cathodes [7, 8].

The cathode manufacturing process has also been investigated to improve cathodic performance in ITSOFC applications. Cathode films are usually fabricated by methods such as screen printing, tape casting, and dry pressing [7-10]. New methods, such as electrophoretic deposition (EPD), have been suggested. EPD involves the formation of a deposited film or layer from particles in stable suspensions. This technique produces films with micron thickness, which is sufficient to maintain good electrochemical performance [11, 12]. The electrochemical performance of cathode composites has been reported [13, 14]. However, for cathode composite LSCF-SDCC that is fabricated by EPD, the effects of sintering temperature on the R_p of the cathode have not been systematically investigated. In the current study, the relation between the sintering temperatures and the parameters could have a significant effect on the cathode's R_p value. The discussed parameters in this study were carbonate content and porosity of the LSCF-SDCC cathode composite film.

EXPERIMENTAL

Materials Preparation

All composite components were purchased from Sigma Aldrich, Malaysia with 99.8 % purity. A mixture of 80 wt. % SDC nanopowder and 20 wt. % carbonates (67 mol. % Li_2CO_3 : 33 mol. % Na_2CO_3) [15] was prepared by ball milling. The SDC, Li_2CO_3, and Na_2CO_3 powders were mixed and ball-milled (Fritsch PULVERISETTE 6, Germany) for 24 h to obtain homogenized composite powders. The mixture was oven-dried and subsequently heat-treated at 680°C for 40 min, thereby forming SDCC. SDCC was then mixed with LSCF at 1:1 weight ratio. The powder mixture underwent ball milling at 550 rpm for 2 h, and the composite mixture was then dried overnight. Subsequently, the composite powders were calcined at 750°C for 2 h [15].

EPD set up

The LSCF-SDCC composite cathode was prepared for cathode film development by EPD process. The LSCF-SDCC composite cathode was prepared at 50:50 weight percentage ratio. An EPD suspension that is based on organic aqueous solution was used, and a mixture of ethanol and deionized water was used as medium. Up to 10 g·l⁻¹ of suspension was prepared, and a dispersing agent, PDADMAC (1 % of the powder weight), was added. EPD was performed on the SDCC electrolyte substrate after suspension preparation. The SDCC electrolyte substrate was obtained by uniaxial press method. The full set up of the EPD process is shown in Figure 1. EPD was conducted at a constant voltage of 20 V with suspension at pH 5, counter electrode size of 50 × 50 mm, and deposition time of 30 min. EPD was conducted on both sides of the substrate surface to obtain a symmetrical cell.
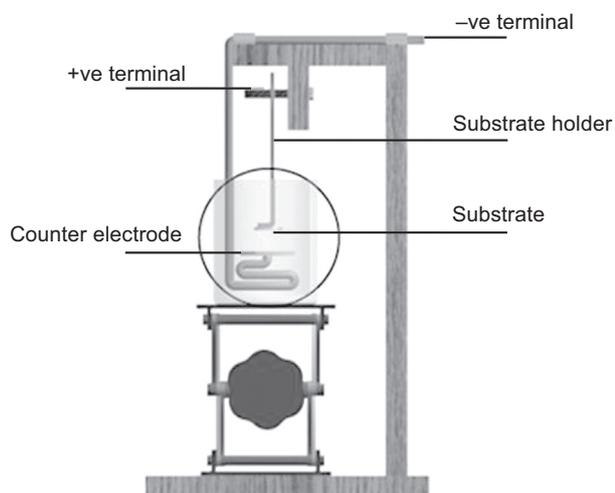

Figure 1. EPD set up.

Characterization method and performance test

The morphology of the sintered cathode film was studied by field-emission (FE) scanning electron microscopy (SEM) (Zeiss Supra 55VP, Germany) coupled with energy dispersive spectroscopy (EDS). EDS was also performed to determine the elemental content in the film. EDS was performed in conjunction with mapping to determine the distribution of carbonate phase in the cathode composite film. Surface porosity values were obtained from the SEM images that were imported into the *Image-J* software.

Symmetrical cells were prepared by painting conductive silver paste on both sides of the cathode. Electrochemical impedance spectroscopy analysis was conducted under static air condition. A symmetrical cell was placed in the middle of a horizontal tube (model 21100, Thermolyne, US) and insulated using alumina plates. The cell was then connected to the potentiostat (model PGSTAT302N, Autolab, Netherlands) alongside a computer with built-in NOVA analysis software (Version 1.8, 2011).

RESULTS AND DISCUSSION

Effect of sintering temperature (T_s) change on elemental content of cathode composite film

The existence of CO_3^{2-} phase in the LSCF-SDCC cathode composite is crucial because the CO_3^{2-} phase functions as a co-ionic conductor (O^{2-} and proton H^+) [16]. However, given the existence of the CO_3^2 phase, the sintering temperatures should be controlled to avoid exceeding the boiling point of CO_3^2 itself. Otherwise, all CO_3^2 phases would be heated up, melted, and would disappear from the composite cathode. Figure 2 shows the result of EDS analysis for the sintered cathode composite film at five different temperatures. After sintering at temperatures of 550, 600, 650, 700, and 750°C, each film still contained all elements (La, Sr, Co, Fe, Sm, Ce, C, and O). EDS analysis showed that the atomic percentage of all sintered elements (except C and O) at different temperatures differed in small amounts. EDS analysis results also showed no undesired peaks that denote the presence of undesired elements in each film after sintering.

Considering that the carbonate in the LSCF-SDCC cathode composite affects the conductivity of ions, the carbonate content was measured in weight percentage. Figure 3 shows the weight percentage of the carbonate phase in each sintered film at 550, 600, 650, 700, and 750°C. From the figure, the carbonate phase decreased with increasing sintering temperature. A significant decrease in weight percentage can be observed in the sintered film at 750°C because the sintering temperature

has reached and exceeded the melting point of Li_2CO_3 (713°C). After powder calcination, the total weight percentage of the carbonate phase was approximately 28 %, which decreased to 23 % after sintering at 750°C. A 5 % loss is considered critical because 1/5 of the original weight had disappeared.

Figure 4 shows the distribution of the carbonate phase in the LSCF-SDCC cathode composite film. Mapping was conducted in conjunction with EDS analysis, and the results are shown in different colors for C and O. The intensity of each color indicates the detected amount of elements in a particular area.
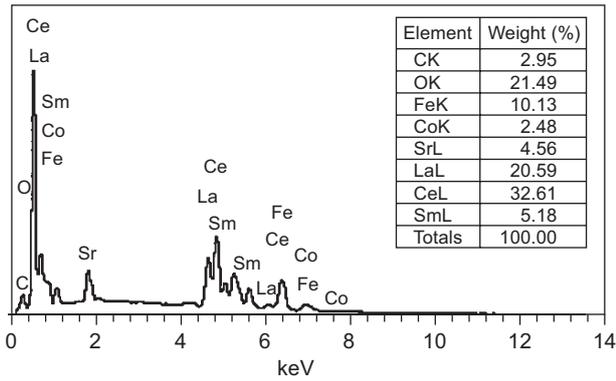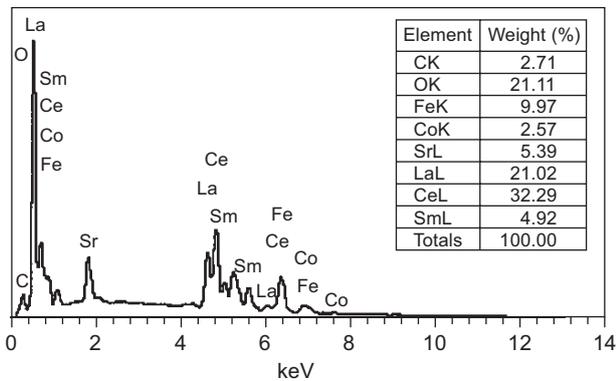
From the obtained mapping result, sintering at 550, 600, and 650°C did not result in any drastic changes in elemental distribution throughout the area. This result is parallel with the amount of weight loss in our previous discussion. However, increasing the sintering temperature to 700°C and 750°C resulted in reduced color intensity of the elements. At 750°C, specific dark spots were observed. These dark areas were formed when the elements melted and disappeared because the temperature reached the boiling point of the elements.
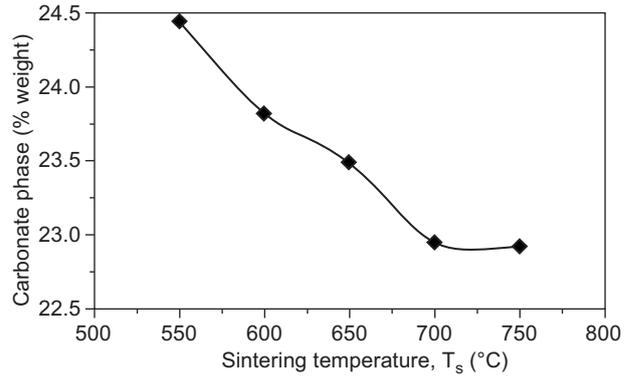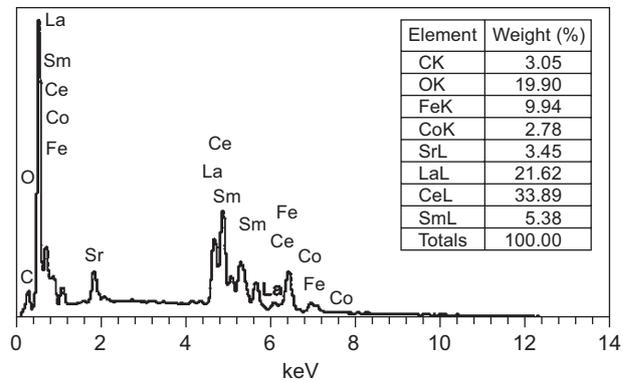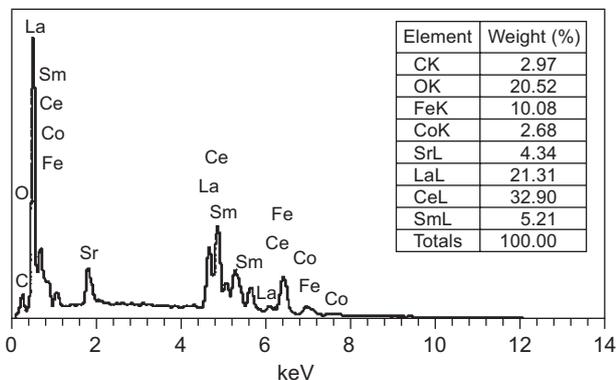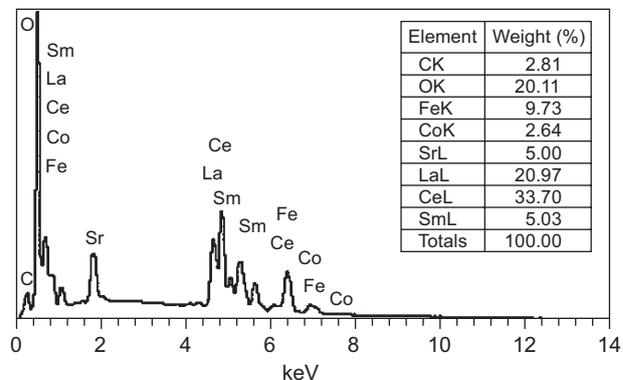

Figure 3. Carbonate content in LSCF-SDCC cathode composite after sintering at five different temperatures.

Element	Weight (%)
CK	2.95
OK	21.49
FeK	10.13
CoK	2.48
SrL	4.56
LaL	20.59
CeL	32.61
SmL	5.18
Totals	100.00

a) 550°C

Element	Weight (%)
CK	2.71
OK	21.11
FeK	9.97
CoK	2.57
SrL	5.39
LaL	21.02
CeL	32.29
SmL	4.92
Totals	100.00

b) 600°C

Element	Weight (%)
CK	3.05
OK	19.90
FeK	9.94
CoK	2.78
SrL	3.45
LaL	21.62
CeL	33.89
SmL	5.38
Totals	100.00

d) 700°C

Element	Weight (%)
CK	2.97
OK	20.52
FeK	10.08
CoK	2.68
SrL	4.34
LaL	21.31
CeL	32.90
SmL	5.21
Totals	100.00

c) 650°C

Element	Weight (%)
CK	2.81
OK	20.11
FeK	9.73
CoK	2.64
SrL	5.00
LaL	20.97
CeL	33.70
SmL	5.03
Totals	100.00

e) 750°C

Figure 2. EDS spectra for all sintered elements in LSCF-SDCC cathode composite at temperatures of: a) 550, b) 600, c) 650, d) 700, and (d) 750°C.

The melted carbonates also flowed in between elements and caused other elements to aggregate, thereby forming large agglomerates. Large agglomerates do not form a packed arrangement. Thus, spots were observed in particular areas.

Effect of sintering temperature (T_s) change on surface porosity of LSCF-SDCC cathode composite film

The sintering temperature has a significant effect on cathode porosity, thereby affecting the cathodic performance. The cathode porosity was analyzed
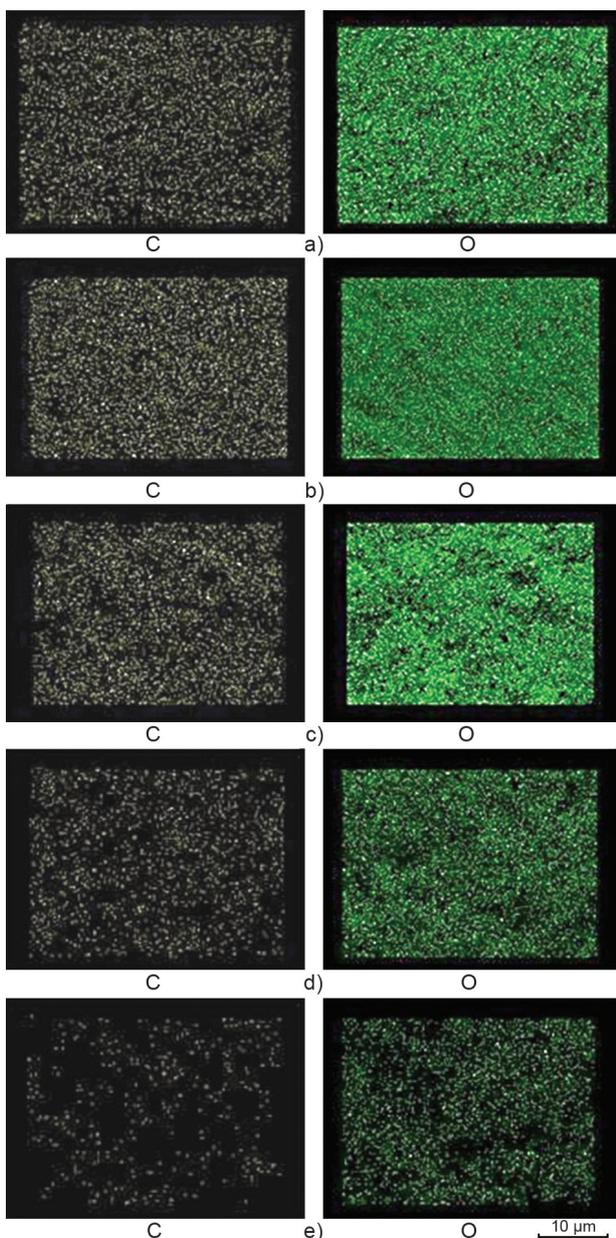

Figure 4. Mapping of elements (C and O) in composite film LSCF-SDCC cathode sintered at 550, 600, 650, 700, and 750°C (scale: 10 μm).

with the assumption that the porosity on the cathode surface is equivalent to the overall film porosity. This assumption was based on the fact that EPD, with the use of a stable suspension, yields homogenously deposited particles [17]. Figure 5 shows the obtained average surface porosity by *Image-J* analysis. The sintered film at 550°C had the highest average surface porosity value. The sintered films at 550, 600, 650, 700, and 750°C yielded porosities of 31.33 ± 0.57 %, 25.89 ± 0.72 %, 24.44 ± 0.85 %, 19.25 ± 0.50 %, and 12.98 ± 0.50 %, respectively. Increasing the sintering temperature caused the carbonate phase to melt, which then tended to cover other elements. Therefore, the elements aggregated and formed large-sized agglomerates. The porosity of the composite cathode decreased because the size of the agglomerates increased with increasing sintering temperature.
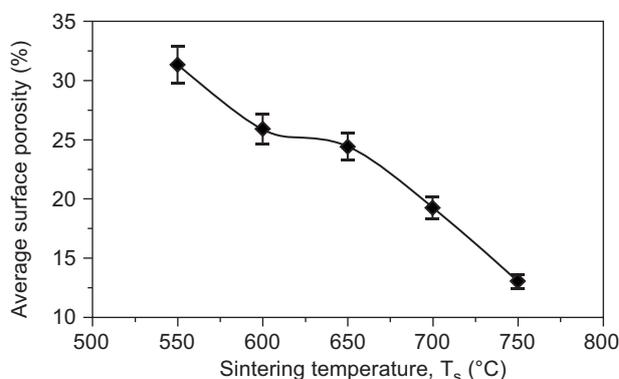

Figure 5. Average surface porosity of sintered LSCF-SDCC cathode composite films at temperatures from 550°C to 750°C.

The practical porosity for the cathode component of IL-LTSOFC is approximately 30 %. Researchers believe that the ionic conductivity of cathodes will improve with this porosity. Several researchers have suggested that the porosity of the cathode should be in the range of 20 % to 40 % to enhance its electrochemical performance [18-21]. In the current study, the optimum sintering temperature for the LSCF-SDCC cathode composite may be selected from 550, 600, and 650°C.

Figure 6 shows the microstructure images of the sintered LSCF-SDCC cathode composites at three sintering temperatures. From the FESEM result, the sintered LSCF-SDCC cathode film at 550°C yielded an average agglomerate size of 0.44 nm, whereas the sintered films at 600°C had an agglomerate size of 0.47 nm. When the sintering temperature was increased to 650°C, the agglomerate size also increased to 0.54 nm. A previous work proposed that after powder calcination, the size of the agglomerates was in the range of 0.4 nm to 0.5 nm [22]. The selected sintering temperatures in the current study (550, 600, and 650°C) did not result in a significant change in agglomerate size because the sintering temperatures were still below the calcination temperature of 750°C.
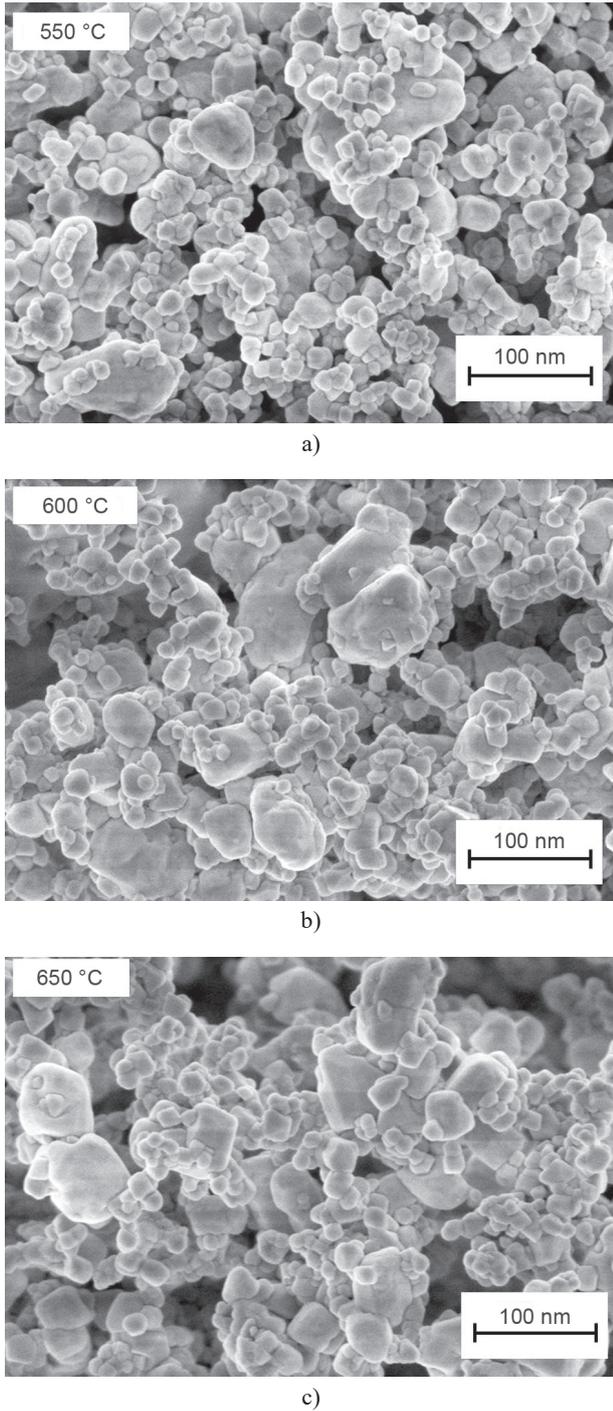
a)

b)

c)

Figure 6. FESEM images of LSCF-SDCC cathode composite surface film after sintering at: a) 550, b) 600, and c) 650°C (scale: 100 nm).

**Effect of sintering temperature (T_s)
change on polarization resistance (R_p) of
LSCF-SDCC cathode composite.**

The sintering temperature has a strong relationship with the electrochemical performance of the cathode. In previous discussions, the relationship between sintering temperature and the existence of a carbonate phase

and porosity of the cathode has been clarified. The electrochemical performance of the cathode was measured by electrochemical impedance spectroscopy (EIS). EIS provides a better understanding of the kinetics and diffusion that occur at the cathode component [13].

Symmetrical cells that were sintered at 550, 600, and 650 °C were subjected to a performance test at five different operating temperatures (450, 500, 550, 600, and 650°C). From the EIS analysis, a Nyquist arc (Figure 7) was constructed. Impedance (*Z* values) was determined from this plotted graph. The R_p was then calculated from the obtained *Z* values from EIS analysis, and an equivalent circuit was also generated. A high R_p value indicates a strong resistance toward ion movement at the cathode, which can result in poor performance of the cathode. An equivalent circuit (Figure 8) was used to obtain the value of R_p. The R_p value is equal to the sum of R_2, R_3, and R_4 [14].
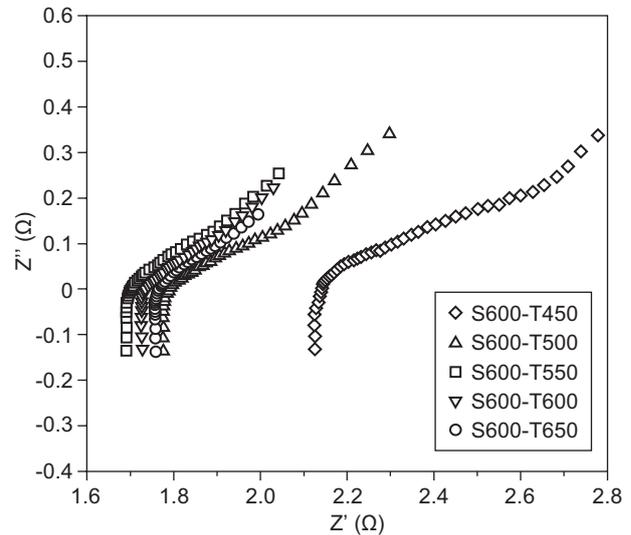

Figure 7. Impedance spectrum of sintered LSCF-SDCC cathode composite symmetrical cell at 600°C (operating temperature of 450°C to 650°C).
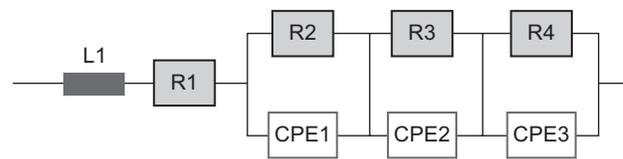

Figure 8. Equivalent circuit for the impedance spectrum of LSCF-SDCC cathode composite symmetrical cell.

Table 1 shows the R_p values for the LSCF-SDCC cathode composite films. The lowest value of R_p was obtained from the sintered cathode at 600°C under an operating temperature of 650°C. The cell with a higher porosity that was sintered at 550°C showed higher R_p value than that of the sintered cell at 600°C. At 600°C,

the effect of ionic conductivity is more dominant than the effect of porosity on the cathode performance. The highest R_p value was obtained with the sintered cell at 650°C which operated at 450°C. These data are attributed to the effect of large-sized agglomerates, which results in a decline in the specific surface area of the reaction. As the area of reaction decreases, the R_p value increases [23].

The lowest R_p value, which was obtained for sintered cells at 600°C (operating temperature of 650°C), indicates that 600°C is the preferred sintering temperature for the LSCF-SDCC cathode composite film.

Table 1. R_p values for sintered LSCF-SDCC cathode composite symmetrical cells at 550°C to 650°C which underwent performance test at temperatures from 450°C to 650°C.

Operating temperature	T_s-550°C	T_s-600°C	T_s-650°C
	R_p (Ω)		
450 °C	4.09	3.15	4.71
500 °C	2.76	2.43	3.68
550 °C	2.28	1.34	3.49
600 °C	1.29	1.15	3.42
650 °C	1.21	0.68	1.61

CONCLUSIONS

This study presented the fabrication of LSCF-SDCC cathode composite film through a new approach, namely, the EPD technique. The effects of sintering temperature on elemental content were analyzed by EDS mapping analysis. From the analysis, all elements still remained in the composite cathode after sintering at temperatures of 550°C to 750°C. Considering that the porosity of the cathode is a crucial factor that affects the sintering temperature, their relationship was also studied. Three sintering temperatures were selected (550, 600, and 650°C) as potential temperatures with corresponding porosity values (20 % to 40 % porosity). The most feasible sintering temperature was determined by conducting EIS to determine the R_p of the cathode. The sintered LSCF-SDCC at 600°C gave the lowest R_p, which was 0.68 Ω when the cathode was operated at 650°C.

Acknowledgments

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