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Characterization and Review of Dual Composite Cathodes LSCF-SDC/YSZ-SDC for Intermediate to Low Temperature Solid Oxide Fuel Cell

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Abstract: Solid oxide fuel cell (SOFC) performance is highly dictated by the ohmic loss of the electrolyte and the resistance due to the cathodic polarization. To reduce the large polarization losses, dual composite cathodes have been introduced. The objectives of this research are to fabricate the LSCF-SDCC/YSZ-SDCC and LSCF-SDC/YSZ-SDC dual composite cathodes powders via ball milling process and evaluate the influence of dual cathode composition and carbonate on the characteristics on physical, morphology and chemical bonding of cathode. In this study, the cathode composite powder is developed from mixture of YSZ-SDC electrolyte powders will be mixed with various ratio 50:50, 60:40 and 70:30 wt%. Powder mixing was done through ball milling method. After mixing, YSZ-SDC electrolyte powders were calcined at 950°C. The morphology of YSZ-SDC powder showed intergranular pores textures are observed at the contact of YSZ and SDC due to SDC lower melting point compared to YSZ which made SDC easily diffuse into YSZ. No additional phase formation is presented in XRD patterns which indicates that there are no crystalline impurities. There is no other chemical bond pattern on side A and B such as carbon. Therefore, YSZ-SDC combination will work together to improve the SOFC conductivity and it is expected to allow the cell operates at intermediate to low temperature.

Keywords: Cathode, LSCF, SDC, SOFC, YSZ

1. Introduction

A power source that will not be exhausted, for instance, solar, wave, geothermal energy and wind energy. The use of fossil fuels used for generating power can be reduced by the use of renewable, which can reduce the greenhouse gas effect. This helps to keep the world safer and greener [1]. Today, one of the concerns of the world community is related to climate change and this leads to the enthusiasm of the world community that changes the perception of low carbon technology that offers cleanliness and

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reliable power for a developing society. SOFC is the most commonly developed because of its high efficiency and its flexibility to use hydrocarbon as well as its versatility in large quantities due to its high efficiency and flexibility [2]. Usually, a fuel cell is made up of anode, cathode and an electrolyte. Many fuel cells are stacked in series connection for real-time applications to produce higher output voltage order SOFC operated at a maximum temperature of 1000℃ [3]. The most recent research has been focused to reduce the operational temperature of the SOFCs by modifying the standard material or by adding new materials which can operate within the low-temperature range (alternatively, 600-800 ° C) and the intermediate temperature range (alternatively, 600 to 1000 ° C). The aim of this research is to evaluate the influence of dual cathode composition on the characteristics based on the physical, morphology and chemical compatibility of cathode through reviewing.

2. Literature Review

2.1 Fuel Cell

Fuel cells are an appealing choice for vehicle applications. Due to their cleanliness, low noise, reliability and performance. However, fuel cells suffer from the slow dynamics induced by the slow transport of reagents, such as the delay in air release (oxygen flow). Fast load changes can lead to destructive fuel starvation and membrane stress. Fuel cell cold start is also difficult as heavy loads have adverse effects during start-up [4].

2.2 Solid Oxide Fuel Cell

SOFCs can produce electricity from different types of fuels for a variety of applications, such as stationary distributed power generation and transport. The primary benefit of the SOFC is its ability to produce it. Electricity at relatively high temperatures as opposed to other fuel cells. For example, high-temperature SOFCs can generate high-quality exhaust heat for co-generation and can be integrated into the gas turbine as the pressure increases to boost the overall efficiency of the SOFC system [5].

2.3 Cathode

Oxygen responds to oxygen ions traveling through the electrolyte with incoming electrons from the external load [6]. The position where oxygen is reduced to oxide ions in each cell is the cathode [7]. The use of a composite cathode, in which an electrolyte material is mixed with the cathode material, is one of the methods for improving cathode efficiency. Lanthanum strontium manganite (LSM), lanthanum strontium ferrite (LSF) and saline sodium citrate (SSC) are widely used cathode materials among these.

3. Methodology

In this study, lanthanum strontium cobalt ferrite (LSCF), samarium doped ceria (SDC) and yttria stabilized zirconia (YSZ) powders were used for the fabrication of composite cathodes LSCF-SDC/YSZ-SDC. These dual composite cathodes were introduced where the LSCF and SDC nano-particles will coat on the YSZ core particles. Table 1 shows the information of composite material use in this study.

Table 1 Composite material used in this study

Materials	Chemical structure	Melting temperature (°C)	Particle size (nm)	Manufacturer
LSCF	$(La_{0.6}Sr_{0.}4)_{0.}97Co0_{.2}Fe_{0.8}O_3$	N/A	400 - 800	KCeracell Co. Ltd. Korea
SDC	$Sm_{0.2}O_{1.9}Ce_{0.8}$	N/A	< 100	
YSZ	$Y_2Zr\ O_5$	>2600	100.0	

KCeracell Co. Ltd.
Korea
KCeracell Co. Ltd.
Korea

3.1 Fabrication of Dual Composite Cathode

The YSZ-SDC electrolyte powders and LSCF-SDC were fabricated by using high energy wet ball milling machine with 550 rpm. The ratio YSZ and SDC materials are 50:50, 60:40 and 70:30 wt% and LSCF and SDC materials are 50:50 wt%. After mixing process, powders YSZ-SDC and LSCF-SDC are dried at 100℃ for 24 hours by using oven. Next, the dried mixture was grounded with agate mortar until a powder form. The YSZ-SDC and LSCF-SDC powders undergone calcination process at temperature 950ºC and 750℃ for 2 hours in electric furnace. However, due to the unexpected global Covid-19 pandemic, only few parts of the planned experiment were able to be carried out. Therefore, journal review on past researches related to the properties (morphology and phase identification) of the dual composite cathodes has been done.

3.2 Charaterisation of SOFC Powder

After the mixing process, characterization of the LSCF-SDC and YSZ-SDC dual composite powders was carried out. Determining their properties is the characterization of the powder by using field emission scanning electron microscopy (FESEM), X-Ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

4. Result and Discussion

4.1 Morphology of calcined YSZ-SDC powder

A scanning electron microscope (SEM) creates an image by scanning a focused electron beam across a surface. The electrons in the beam interact with the sample, producing a variety of signals that can be used to determine the surface topography and composition. Figure 1 shows the morphology of YSZ-SDC powder with 50:50 wt%, 60:40 wt% and 70:30 wt% that has been calcined at temperature 950℃ with the magnification of 1000x.

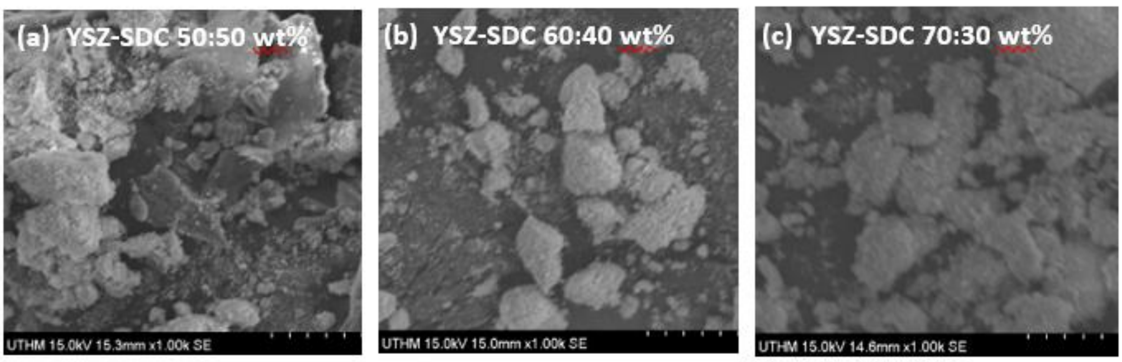


Figure 1 SEM morphologies of calcined (a) YSZ-SDC 50:50 wt%, (b) YSZ-SDC 60:40 wt% and YSZ-SDC 70:30 wt% at temperature 950℃

As shown in Figure 1 (a), (b) and (c), agglomerates pores textures are observed where pores are at the contact of YSZ and SDC due to SDC lower melting point compared to YSZ made SDC easily diffuse into YSZ. This phenomenon was reported based on the previous study [8].

4.2 Phase Identification of calcined YSZ-SDC powder

In this section, XRD test was perform to identify the phase of the calcined YSZ-SDC powder with different ratio of wt% meets with the YSZ and SDC powder peak. Figure 2 shows the XRD patterns of the SDC (JCPDS card no.75-0157), YSZ (JCPDS card no. 30-1468) and calcined YSZ-SDC wt% of 50:50, 60:40, 70:30 powder.

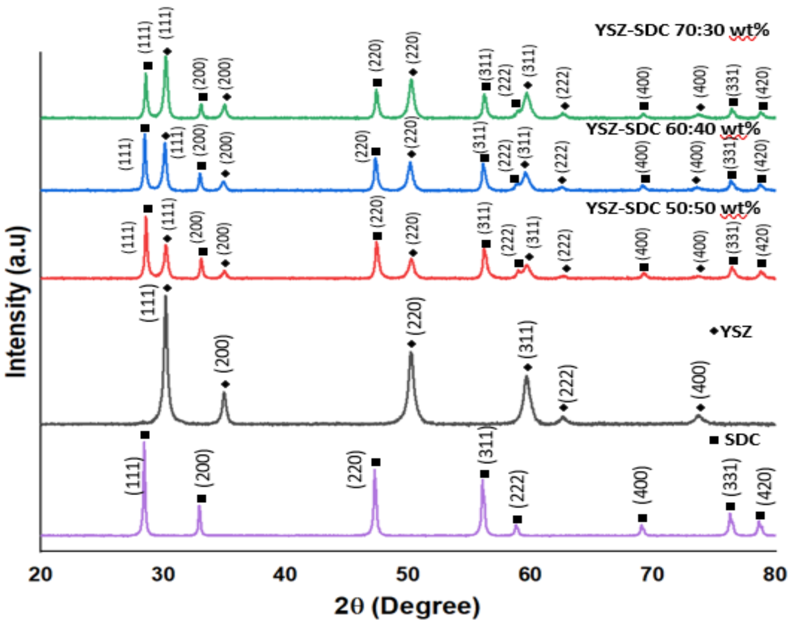


Figure 2 XRD pattern of calcined SDC, YSZ and YSZ-SDC powder with composition 50:50, 60:40 and 70:30 wt%

Table 2 Various parameters of SDC, YSZ, YSZ-SDC 50:50, 60:40 and 70:30 wt%

Composition	Lattice constant (a) from JCPDS num.	Lattice constant (a) from calculation	Average crystallite size (nm)
SDC	5.4230	5.1390	30.6052
YSZ	5.4315	5.1300	15.3059
YSZ-SDC 50:50 wt%	-	5.2930	21.5477
YSZ-SDC 60:40 wt%	-	5.3023	22.3527
YSZ-SDC 70:30 wt%	-	5.2944	22.4039

Based on the XRD analysis obtained in Figure 2, the peaks of YSZ-SDC 50:50, 60:40 and 70:30 wt% matched with the XRD profiles of YSZ and SDC powder. There is no additional or secondary phase formation is present in XRD patterns which indicates that there are no impurities. The intensity of the diffraction peaks of YSZ-SDC powders increased with increasing of YSZ and intensity of the diffraction of YSZ-SDC decreased with decreasing of SDC. This show that the crystallinity of the SDC powders decreased with increasing of YSZ. As shown in Table 2, the lattice constant value of SDC and

YSZ that obtain from JCPDS number data is 5.4230 and 5.1390. From the theoretical that has been made using Scherrer's Equation, Bragg's Law and interplanar equation for cubic, the average value of lattice constant for SDC and YSZ is 5.4315 and 5.1300. The calculated values of lattice constant are not much different from the theoretical (database) value. This shows that the cubic size is a bit smaller compare to the original data from JCPDS number [9].

4.3 Chemical bonding of calcined YSZ-SDC powder

FTIR test was performed in order to identify chemical bonding of YSZ, SDC and calcined YSZ-SDC powder with ratio of 50:50, 60:40 and 70:30 wt%. Figure 3 shows the FTIR patterns of the SDC, YSZ and calcined YSZ-SDC 50:50, 60:40 and 70:30 wt%. The IR spectrum used is mid-IR spectrum where the wavenumber is in between 400-4000 cm-1.

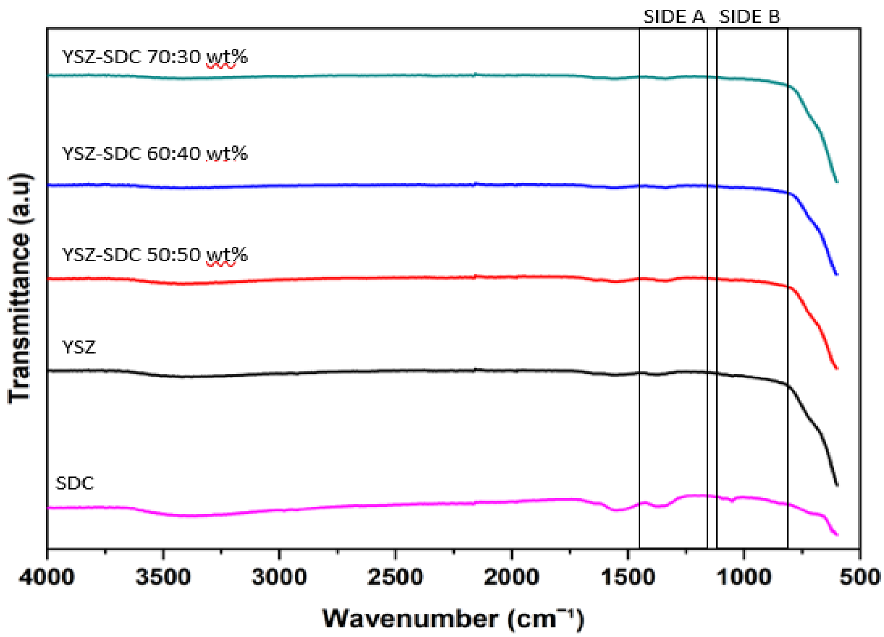
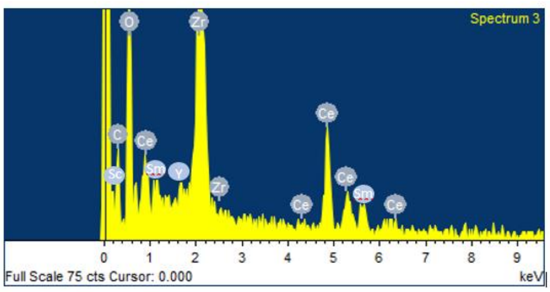


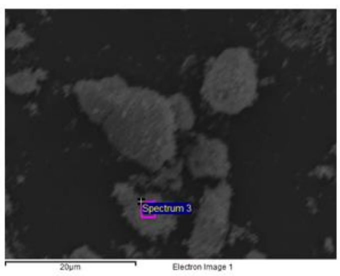
Figure 3 FTIR pattern of calcined SDC, YSZ and YSZ-SDC powder

Based on the FTIR result obtained in Figure 3, there is no other chemical bond pattern on side A and B such as carbon. This is due to SDC which is easily diffuse into YSZ and perform a pure YSZ-SDC mixture in a different wight percentage ratio. There is no peak obtained on side A and B from YSZ and YSZ-SDC powders. This can be analysed that this is a simple chemical. No single, double and triple bond region was detected, informing there is no C=C bond in the material.

4.4 Element Identification in YSZ-SDC powder

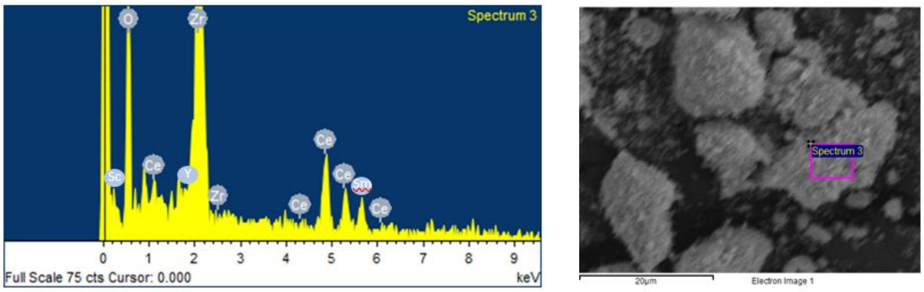
The elements distribution of powders was showed under EDS-SEM testing machine. EDS-SEM machine able to determine all the elements of composite of SOFC. Each composite should contain elements yttria (Y), zirconium (Zr), samarium (Sm), scandium (Sc) and cerium (Ce). In Figure 4 to 6, it shows the element in each composite which is oxygen (O), zirconium (Zr) and cerium (Cr).





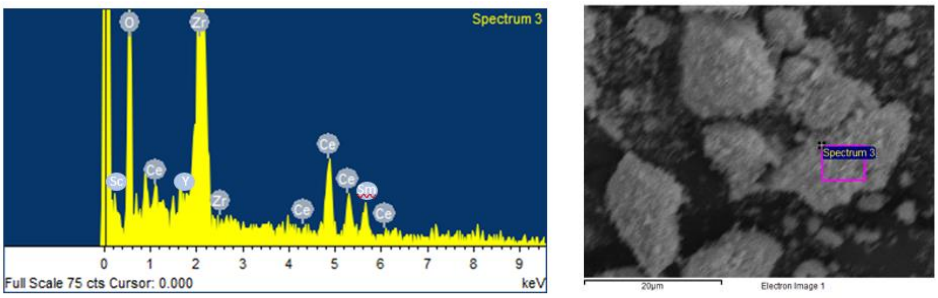
Element	Weight%	Atomic%
C K	11.98	27.84
O K	33.59	58.60
Zr L	25.36	7.76
Ce L	29.08	5.79
Totals	100.00	

Figure 4 EDS distribution for calcined YSZ-SDC 50:50 wt%



Element	Weight%	Atomic%
O K	32.98	76.63
Zr L	39.33	16.03
Ce L	27.69	7.35
Totals	100.00	

Figure 5 EDS distribution for calcined YSZ-SDC 60:40 wt%



Element	Weight%	Atomic%
O K	32.98	76.63
Zr L	39.33	16.03
Ce L	27.69	7.35
Totals	100.00	

Figure 6 EDS distribution for calcined YSZ-SDC 70:30 wt%

4.5 Review on morphology of calcined LSCF-SDC powder

Particle morphology of the prepared cathode powder of LSCF and LSCF–SDC were analysed using a FESEM at magnification of (50,000x), as shown in Figure 7. LSCF powders were presented with a heterogeneous particle size distribution ranging from 45 to 65 nm in particle size. The two constituent materials, LSCF and SDC, are clearly separated by the microstructure of the LSCF–SDC composite cathode, as seen in Figure 7(b). SDC has a coarse microstructure. Generally, a coarse microstructure makes gas transportation and enhances conductivity through ion and electronics. The calcined LSCF and LSCF–SDC cathode composite powders are shown in Table 3 [10].

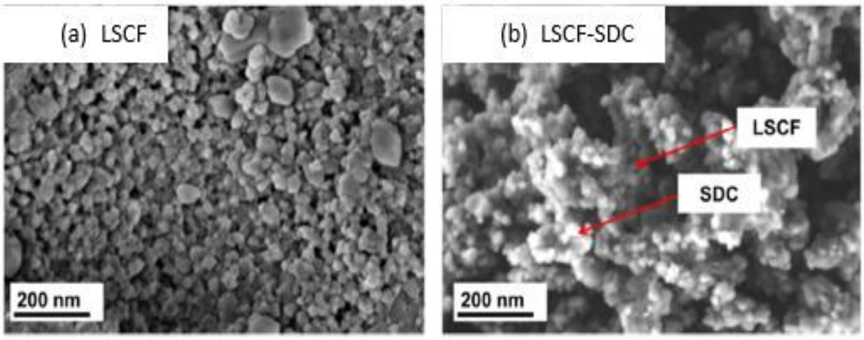


Figure 7 FESEM images of calcined (a) LSCF and (b) LSCF-SDC of 50:50 wt% powder at 700℃ [10]

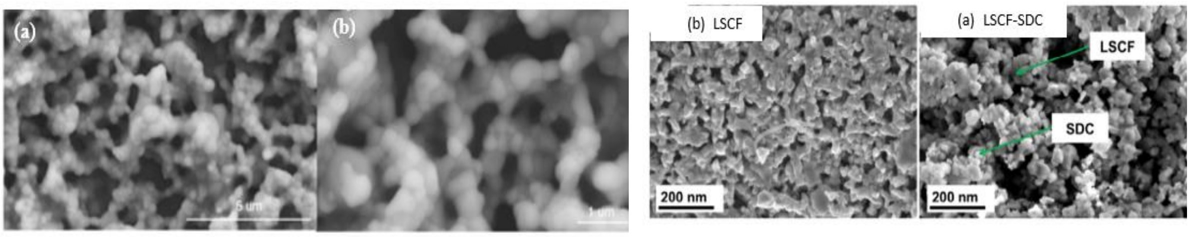


Figure 8 SEM images for calcined LSCF-SDC with 50:50 wt% (a) and (b) view powder with different magnification at 1150°C [11].

Figure 9 SEM images for calcined (a) LSCF and (b) LSCF-SDC with 50:50 wt% powder at 1000°C [12].

Table 3 XRD and BET results of calcined LSCF and LSCF–SDC composite cathode powders [10].

Properties	LSCF	SDC	LSCF/SDC	
			LSCF	SDC
Structure	Rhombohedral	Cubic	Rhombohedral	Cubic
Space group	R-3C (167)	Fm-3m (225)	R-3C (167)	Fm-3m (225)
D_{XRD} (nm)	33.8 (110)	67.2 (111)	33.8 (110)	83.7 (111)
a (Å)	5.49	5.43	5.49	5.41
c (Å)	13.41		13.41	
ρ_{Thd} (g/cm^3)	6.33	7.21	6.33	7.34
S_{BET} (m^2/g)	14.4	10-14	7.6	

The area of the composites cathode is shown as Figures 8 (a) and (b) indicate that it is made up of submicron grain agglomerates. Moreover, an open microstructure and highly linked network is observed, which might allow oxygen molecules to be diffused via the gas phase in the TPB areas [11]. The FESEM analysis examined and recorded the microstructure of the produced LSCF and LSCF-SDC composites with a high magnitude of 50,000 TB as shown in Figure 9 (a) and (b). Although both prepared powders were structured and crystallised identically, their microstructure had different particle sizes, agglomeration levels and particle aggregation. As a sponge-like, the LSCF powder emerged, and the particles were connected as agglomerates as shown in Figure 9(a). The SDC in the LSCF-SDC composite is homogeneously mixed with LSCF and a continuous LSCF-SDC network together with a very porous structure is formed as illustrated in Figure 9(b) [12].

Based on the review that has been made, the expected result of morphological for calcined LSCF-SDC with 50:50 wt% at temperature 750°C can be predicted. From the review result for temperature 700°C [10], 1000°C [12] and 1150°C [11] shows that the microstructure is highly linked network. From the review result, the expected result this study for LSCF-SDC microstructure temperature at 750°C might be in the form of connected each other. The expected result texture of the powders can be in the form of agglomerates and the particles feasible in aggregates and uniformly distributed. This is based on the study of Loureiro and Muhammed Ali.

4.6 Review on phase identification of calcined LSCF-SDC powder

LSCF03, LSCF06 were sintered at 900 °C for 6 h in air. Findings from the experiments (Figure 10) showed that all sample peaks were indexed as cubic perovskite type structures without impurities except LCSCF09. Two peaks at 2θ around 27° and 57° indicated the formation of the second phase of CeO2 in the LCSCF09 sample. The second phase in LCSCF09 indicates that Ce was not successfully incorporated into the LSCF A site. As seen in Figure 10, the peaks shift to a lower angle with increasing Ce content, indicating that the lattice parameters are enlarged [13].

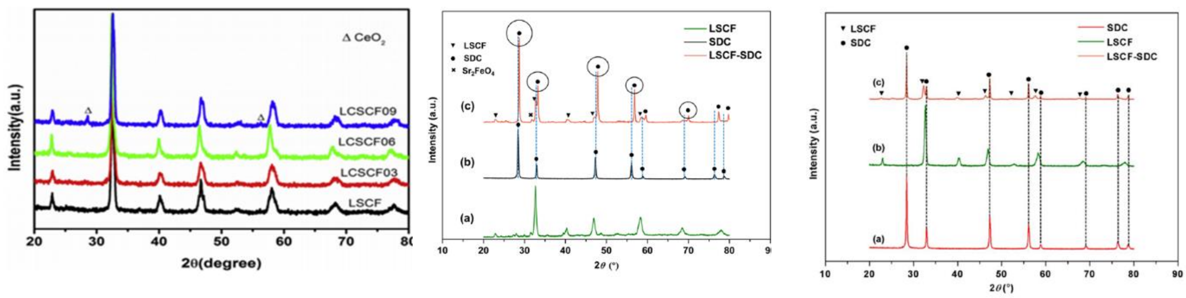


Figure 10 XRD patterns of doping Ce_x on LSCF [13]

Figure 11 XRD patterns of calcined LSCF, SDC and LSCF-SDC powder with 50:50 wt% at 700℃ [10]

Figure 12 XRD pattern of calcined LSCF-SDC powder with 50:50 wt% at 1000℃ [12]

Figure 11 displays the XRD patterns for the composite cathode SDC and LSCF–SDC. The LSCF–SDC composite powders were made of XRD and showed no phase changes, and ceria and LSCF peaks. The standard peaks of perovskite LSCF (space group R-3C (167), JPCDS PDF# 01-081-9113) and cubic fluorite SDC (space group Fm-3m (225), JPCDS PDF# 00-034-0394) were discovered, which demonstrated outstanding chemical compatibility in mixtures and calcinations. The standard peaks have been discovered. SDC showed no phase change and had just a pure cerianite (CeO2) cubic fluorite structure for composite powders. The crystal structure of the SDC lattice distortion in the LSCF–SDC composite cathode displayed a tensile strain. To determine the distortion in crystal properties, the main peak (111) of SDC powders was analysed [10].

Figure 12 (a–c) shows the phase structures of SDC, LSCF, and LSCF–SDC composite powders. Figure 12(b) shows a single pure perovskite-type structured LSCF without any other phases in the LSCF powder. Figure 12(c) shows that the LSCF–SDC composite powders had a stable structure and that the XRD pattern had not changed much. The LSCF–SDC composite powders' XRD pattern consisted of ceria and LSCF peaks, with no evidence of phase alteration or shift in peak locations [12].

According to recent studies result of XRD for calcined LSCF-SDC powder with 50:50 wt% and temperature between 700℃ to 1050℃ shows that the figure of the XRD pattern is clearly can be observed that there was no other chemical reaction and secondary peaks occurs between LSCF and SDC [10], [14]. This shows that LSCF and SDC that calcined at temperature between 700℃ to 1050℃ with 50:50 wt% produced a great chemical compatibility over mixing and calcination. Therefore, for the expected result of XRD for calcined LSCF-SDC at temperature 750℃ with 50:50 wt% might not produce secondary peaks or other chemical reaction in between LSCF and SDC. This may be because the XRD peaks produced by the calcined LSCF-SDC powder have no significant difference between pure LSCF and SDC. This proves that LSCF-SDC has good chemical compatibility. In short, continued and improved need to be done in order to determine the crystallite size by using Scherrer's Equation.

5. Conclusion

The aim of this study is to evaluate the influence of composite cathode composition on the characteristics (physical, morphological and chemical suitability) of the cathode. In this study, the characterisations for YSZ-SDC were successfully obtained and achieved. Characterisations for powder LSCF-SDC were observed based on review process. According to the previous study, YSZ-SDC composite cathode is highly improved electrical conductivity was obtained in the composite material in composition of weight ratio 85:15. In this study, for the composition of weight ratio 70:30 show the improvement of electrical conductivity compared to the other composition respectively. For LSCF-SDC composite cathode from the review shows LSCF is mixed mechanically with SDC because the cathode lowers the electrochemical performance of the half-cell. This cathode also shows clear microstructural differences at the cathode/interconnection. The morphology shows that the powders form a large aggregates texture and the particle size exceed the crystallite size. Based on the phase identification, it is clearly showing that there was no other phase and secondary formation produced from the LSCF-SDC powders prove that the powders had a stable structure. From this study the suitable amount of percentage composition of weight for YSZ-SDC cathode powder are between 50:50,60:40 and 70:30. The LSCF/YSZ-SDC is expected to exhibit good physical, morphology and chemical stability for the application of intermediate to low temperature SOFC.

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