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Phase Stability of LSCF/YSZ- SDC & LSCF/YSZ-SDCC Dual Composite Cathode Solid Oxide Fuel Cell

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Abstract: This study presents the preparation of two types of dual composite cathode for solid oxide fuel cell (SOFC). Lanthanum Strontium Cobalt Ferrite (LSCF)/ Yttria Stabilized Zirconia (YSZ)-Samarium doped ceria (SDC) and Lanthanum Strontium Cobalt Ferrite (LSCF)/ Yttria Stabilized Zirconia (YSZ)-Samarium doped ceria carbonate (SDCC). The aims for this study are to investigate the initial stage compatibility of phase stability between the cathode and electrolyte material. Commercial powder LSCF was mixed with composite powder YSZ-SDC and YSZ-SDCC by ball milling at 550 rpm for 2 hours. Subsequently, the dual composite cathode powders were calcined at 750℃ for 1 hours. The behavior of LSCF/YSZ-SDC and LSCF/YSZ-SDCC dual composite cathode powders was characterized via X-ray Diffraction to determine the crystalline phase of dual composite after several process have acted on the powder. Nondestructive testing method, Fourier transform infrared spectroscopy was used to determine the existence of carbonate bond in LSCF/YSZ-SDCC powders. The finding shows that LSCF/YSZ-SDC and LSCF/YSZ-SDCC preliminary phase stability are compatible and suitable to proceed the next step.

Keywords: Dual Composite Cathode, LSCF, SDCC, SOFC, YSZ

1. Introduction

Fuel cells produce electrical work directly from chemical energy by combining the fuel and oxidant electrochemically [1]. In principle, SOFCs energy system is simpler, flexibility and versatility fuel. Moreover, SOFCs have high energy efficiency compared to the other [2]. Three main components in SOFC system are cathode, anode and electrolyte. Oxygen reduction occurs at the cathode. Oxygen dissociates through cathode to form O^{2-} ion. O^{2-} migrate to the anode through a dense electrolyte and react with H_2 in the fuel to produce of SOFC [3]. The most attractive material for cathode electrode is perovskites material. Especially materials contents mixed ionic and electronic conductors (MIECs) [4].

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These factors have attracted the researchers especially in SOFC studies as it can be applied in cathodes component for excellent oxygen separation membrane and catalytic conversion [5].

LSCF, the ferrite-based perovskites are a promising MIEC material as it can increase the ionic and electronic conductivity by substituting cations on the lanthanum and cobalt site [6]. LSCF also an ideal material to operating at intermediate to low temperature due to the perovskite (ABO_3) structure-type MIEC factors [6]. In addition, LSCF was proved to have an excellent chemical and thermal compatibility with doped ceria electrolytes especially with samarium-doped ceria [7-8]. Most importantly, samarium-doped ceria was listed as a promising electrolyte material for reducing the operating temperature in SOFC application [7]. However, LSCF perovskites cathode still facing several issues even have the good compatibility with doped ceria electrolyte such as resulted in severe microstructural and suffer structural degradation at temperature 600℃ above under full operation [9]. As a suggestion addition of carbonate salts (Li_2 / Na_2) in cathode components can improve the overall performance of the low temperature solid oxide fuel cell [5].

Yttria dopants was added to stabilize the high temperature structures to low temperature by forming a chemical reaction with ZrO_2[2]. Composition of the yttria-stabilized zirconia will affect the cathode conductivity [2]. The increasing of the conductivity is due to the increase of charge carriers [2]. Phase stability of cathode is one of important factor to enhance the performance cells. Taking all the advantages from LSCF, YSZ, SDC and carbonates salts into account, it is expected to augment an excellent dual composites cathode.

2. Materials and Methods

Commercial powders LSCF, YSZ and SDC (Kceracell, Korea) were used as the main material in this study. Added Samarium Doped Ceria Carbonate (SDCC) was prepared by wet ball milling method using high energy ball milling machine (Pulverisette 6, Fristch, Germany) at low speed (150rpm) for 24 hours. SDCC composite powder was formulated using 80wt% SDC raw powder and 20wt% of binary carbonates (67mol% Li_2CO_3: 33 mol % Na_2CO_3) followed by calcination process at 680℃ for two hours with heating and cooling rate 5℃/min. Commercial powder YSZ was mixed with SDC and SDCC composite powder at three different compositions (50wt%: 50wt%, 60wt%: 40wt% and 70wt%: 30wt%). Composite powders YSZ-SDC and YSZ-SDCC were calcined at 950℃ and 680℃ respectively. For dual composite powders formulation, a commercial LSCF powders was mixing together with of YSZ-SDC and YSZ-SDCC composite powders by high-speed ball milling method for 550 rpm speed with 2 hours at 1:1 weight ratio and proceed with calcination at 750℃ for 1 hour. Table 1 and Table 2 shows the abbreviation of composite powder and dual composite powder with its parameters.

Table 1. YSZ-SDC and YSZ-SDCC composites powders Composition

Sample	Composite Powders	Weight Ratio Composition (wt.%: wt.%)
Y-S1	YSZ-SDC	50:50
Y-S2	YSZ-SDC	60:40
Y-S3	YSZ-SDC	70:30
Y-SC1	YSZ-SDCC	50:50
Y-SC2	YSZ-SDCC	60:40
Y-SC3	YSZ-SDCC	70:30

Table 2. Dual composites powders and weight ratio composition.

Sample	Dual Composite Powder	Weight Ratio Composition (wt.%)

LS/Y-S1	LSCF/YSZ-SDC	50/50:50
LS/Y-S2	LSCF/YSZ-SDC	50/60:40
LS/Y-S3	LSCF/YSZ-SDC	50/70:30
LS/Y-SC1	LSCF/YSZ-SDCC	50/50:50
LS/Y-SC2	LSCF/YSZ-SDCC	50/60:40
LS/Y-SC3	LSCF/YSZ-SDCC	50/70:30

Phase identification for composites powders and dual composites powders were characterized by using X-ray diffraction (XRD) machine (Brucker D8 Advance, Germany) with Cu Kα emission radiation at 0.15418 nm wavelength (λ=0.15418) using a scanning of 2θ in the angle range between (20° to 80°). The crystalline phase for all the powders involves were examined to ensure good crystalline phase without any contamination or second phase appear. Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 100, USA) was performed to identify the existence of carbonates. The samples are analyzed using spectrum express version 1.3.2 software within the spectral range 4000-600 cm^{-1}. Surface morphology and element distribution of samples powders were examined using Field Emission Scanning Electron Microscopy (FESEM) connected with Energy Dispersive Spectroscopy (EDS). Small amounts of samples powders were spreads on copper tape attached to sample holder, coated with thin film of gold. The process was performed in Secondary Electron Imaging (SEI) mode using an accelerating voltage of 5 keV. Images at higher magnification were collected.

3. Results and Discussion

3.1 Phase Analysis

The phase compatibility between SDC, Carbonate, YSZ electrolyte and LSCF cathode materials was influenced by the processing technique such as synthesis method, heat treatment and applied temperature [5]. The phase compatibility for LSCF/YSZ-SDC and LSCF/YSZ-SDCC dual composites cathode powders analyzed through XRD that could determine the phase and crystal structure. Fig.1 and Fig.2 display the x-ray pattern of YSZ composites with different weight of composition. SDC (JCPDS No 01-075-0157) and YSZ (JCPDS No 00-030-1468) were detected for composites powders prepared. X-ray pattern for YSZ composites shows the crystallite peak for SDC phase. This implies that SDC forms well-defined fluorite crystal structure while carbonates form amorphous structure [sf Mohamad et al 2019]. From Fig. 1 and Fig.2 the intensity for the YSZ is increasing as the ratio of composition increase same goes to SDC and SDCC intensity are declined when the composition ratio is reduced. The YSZ and LSCF composites were compared with the commercial YSZ, SDC and LSCF peaks. As seen in Fig.1, Fig.2, Fig. 3 and Fig. 4 only the primary phases including the LSCF perovskite, YSZ cubic and SDC cubic phase were detected without any impurity form. This proves that the wet milling method can prevents the secondary phases.

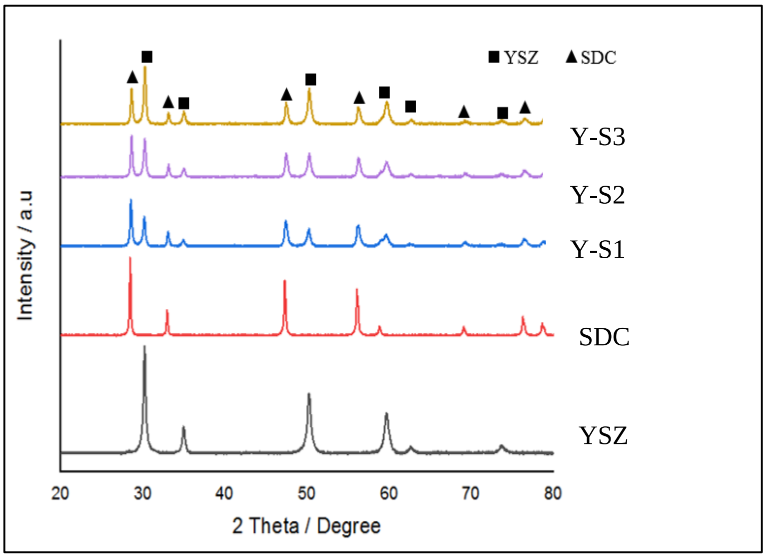

Figure 1: XRD analysis for YSZ-SDC composites

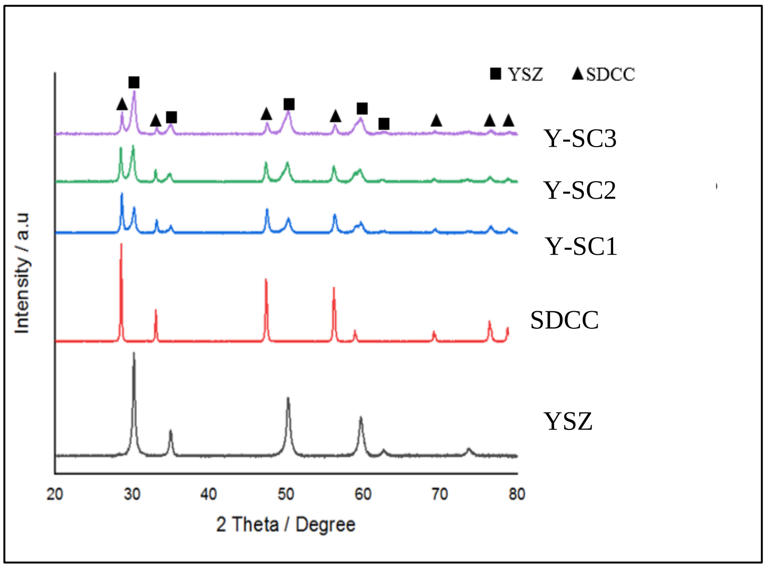

Figure 2: XRD analysis for YSZ-SDCC composites

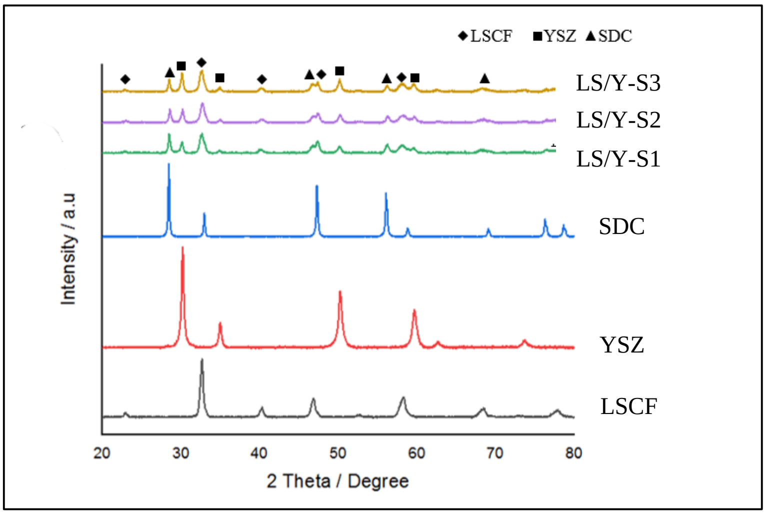

Figure 3: XRD analysis for LSCF/YSZ-SDC

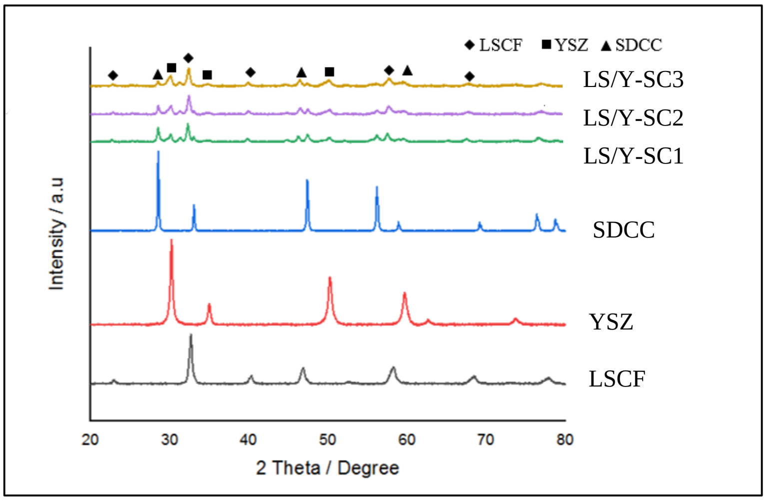

Figure 4: XRD analysis for LSCF/YSZ-SDCC

LSCF phase (JCPDS No 01-089-5720) in Fig 3. and Fig. 4 show the declined intensity and broadened width due to the addition of LSCF as dual composites. However, a small decrease in peak intensity still represented a better structural and crystallization formation. To present the better result for production of dual composites powders, average crystallite size of the powders for each composition composites was calculated by using the following equation (1) proposed by Paul Scherrer [11].

$$\text{Crystallites Size Powder (nm)} = \frac{K\lambda}{\beta cos\theta} \qquad \text{Eq.1}$$

where K= 0.9 (Scherrer constant), λ=0.15418 (wavelength of the x-ray sources), β=FWHM (Full Width at Half Maximum) and θ= Bragg angle (Peak position).

The smaller the crystallite size, the broadened the peak width [11]. Analyzed collected clarified that size of the crystallite is an important fundamental factor for the cathode conductivity during the performance of the cell [12]. The grain size or crystallite size must smaller than 100nm and comes with homogenous nanostructured as it can help to enhance the performance and improving the long-term stability of the SOFC cells. [13] Table 3 shows that the crystallite size for LSCF and YSZ reducing in LS/Y-S1, LS/Y-S2, LS/Y-S3, LS/Y-SC1, LS/Y-SC2 and LS/Y-SC3 since broaden of the peak width. Meanwhile, SDC peak shows a contradict result when the LS/Y-S1 shows a smallest crystallite size follow by LS/Y-S2 and LS/Y-S3. Crystallite size SDCC for LS/Y-SC3 displays the smallest crystallite compared to LS/Y-SC2 and LS/Y-SC3. Considering the incorporation of $(LiNa)_2$carbonate during the milling process probably due to lower amount SDCC percentage added.

Table 3. Crystallite size of dual composites powders cathode

Samples	Average Crystallite Size (nm)					
	Y-S1	**Y-S2**	**Y-S3**	**Y-SC1**	**Y-SC2**	**Y-SC3**
YSZ	16.21	15.07	17.29	12.33	11.52	10.04
SDC	18.05	17.32	20.38	-	-	-
SDCC	-	-	-	21.13	21.96	19.51

Samples	Average Crystallite Size (nm)					
	LS/Y-S1	**LS/Y-S2**	**LS/Y-S3**	**LS/Y-SC1**	**LS/Y-SC2**	**LS/Y-SC3**
LSCF	14.69	13.09	12.34	16.59	15.47	15.36
YSZ	18.57	18.33	13.21	20.69	18.91	16.45
SDC	12.01	15.24	16.88	-	-	-

SDCC	-	-	-	20.32	19.62	11.58

3.2 Chemical Bonding Analysis

FTIR spectroscopy was performed to identify the existence of carbonates bond in YSZ composites cathode and LSCF dual composites cathode. Infrared spectra in Fig. 5 shows the presents of carbonate bonds in YSZ-SDCC composites samples. The carbonate bond for Y-SC1, Y-SC2 and Y-SC3 were detected at 1504 cm^{-1} to 861 cm^{-1}, 1504 cm^{-1} to 861 cm^{-1} and 1510 cm^{-1} to 861 cm^{-1} respectively. This finding was supported by previous finding which it stated that $CO_3{}^2$ was observed at 1530-1320 cm^{-1} and 860 cm^{-1} .

Fig. 6 displays the FTIR spectra for LSCF dual composites after milling together with YSZ composites. The carbonates bond was confirmed for LS/Y-SC1, LS/Y-SC2 and LS/Y-SC3 at 1445 cm^{-1}, 1444 cm^{-1} and 1447 cm^{-1} respectively. Despite that, LS/Y-S1, LS/Y-S2 and LS/Y-S3 also detected a small curve around the carbonates bond site. This remarkable was considering as the chemical reaction product between LSCF and YSZ, $La_2Zr_2O_7$ and $SrZrO_3$ [14].

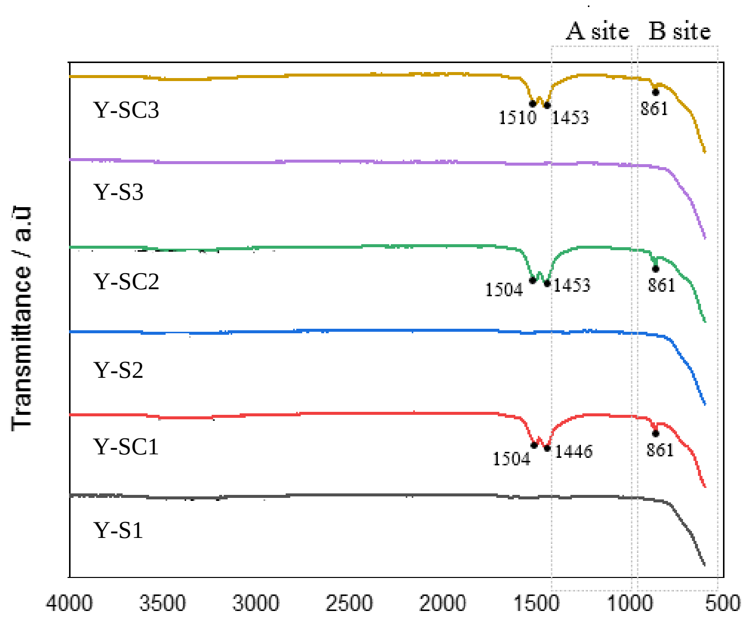

Figure 5: FTIR spectra for YSZ-SDC and YSZ-SDCC composites

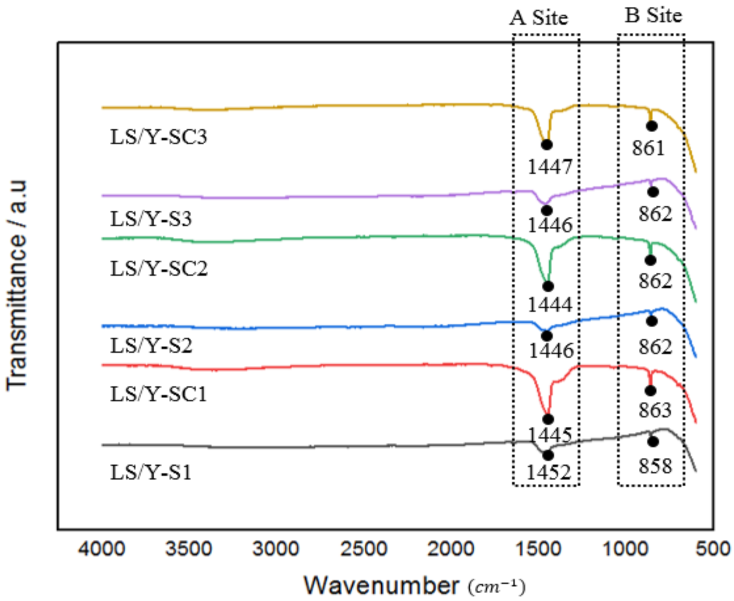

Figure 6: FTIR spectra for LSCF dual composites

3.3 Morphology Analysis and Element Distribution of Dual Composites Powder

The nano-sized particles were observed by FESEM from the dual composites powder samples. Fig.7 (a) and (c) show the result for composite powders without the addition of the carbonate salt while Fig. 7 (b) and (d) are the surface morphology result for the composite powders with the addition of the Li_2CO_3 and Na_2CO_3. It is seen on FESEM images that the particles are homogenous and stick together especially in Fig.7 (b), (c) and (d) the particles are in agglomeration state. The average particles size of (50:50) wt.% YSZ-SDC and YSZ-SDCC composition in Fig.7 (a) and (b) after analyzed by Image J software reveal to be 375 µm and 441 µm respectively. In addition, the develop (50/ 50:50) wt.% dual composite powder, LSCF/YSZ-SDC and LSCF/YSZ-SDCC average particles size are increasing to 389 µm and 447µm. The increase in particles size was expected as attributed to the calcination process.

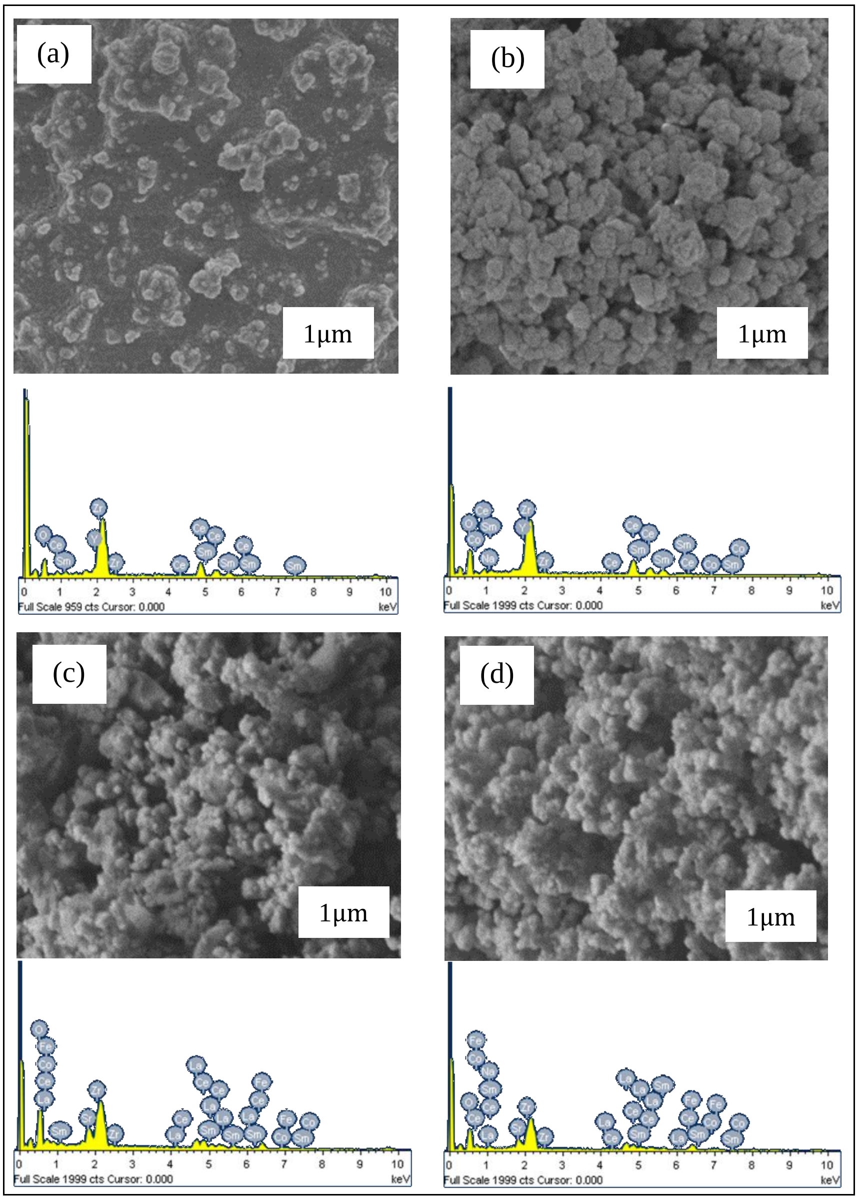

Figure 7: FESEM images of composites powder and dual composites powder (a) YSZ-SDC (b) YSZ-SDCC (c) LSCF/YSZ-SDC (d) LSCF/YSZ-SDCC

The EDS pattern for YSZ composites and LSCF dual composites are shown in Fig.7 as well. The figures shown the presence of yttrium (Y), zirconium (Zr), samarium (Sm), cerium (Ce) and oxygen (O) for Fig, 7 (a) meanwhile the presence of sodium (Na) and cobalt (Co) are detected in Fig. 7 (b) due to the addition of lithium carbonate and sodium carbonate for the mixing of SDCC. At the same time, lithium (Li) was not detected because it has low energy of characteristics radiation [15]. In Fig.7 (c) and (d) the elements that was detected are lanthanum (La), strontium (Sr), cobalt (Co), iron (Fe), zirconium (Zr), samarium (Sm), cerium (Ce), sodium (Na) and oxygen (O) respectively. Details of elements percentage for each composite powder is listed in Table 4 and Table 5 below.

Table 4: Atomic percentage for YSZ-SDC and YSZ-SDCC

Elements Fig,7 (a) (YSZ-SDC)	Atomic (%)	Elements Fig.7 (b) (YSZ-SDCC)	Atomic (%)
Y	0.05	Y	2.60
Zr	16.19	Zr	18.33
Sm	2.58	Sm	2.32
Ce	19.12	Ce	12.57
O	62.06	Na	0.78
		Co	0.14
		O	63.27
Total	100%	Total	100%

Table 5: Atomic percentage for LSCF/YSZ-SDC and LSCF/YSZ-SDCC

Elements Fig,7 (c) (LSCF/YSZ-SDC)	Atomic (%)	Elements Fig.7 (d) (LSCF/YSZ-SDCC)	Atomic (%)
La	5.61	La	7.41
Sr	5.42	Sr	5.03
Fe	6.79	Fe	12.73
Co	1.82	Co	2.47
Zr	6.05	Zr	4.40
Sm	1.24	Sm	1.38
Ce	5.79	Ce	6.25
O	67.28	Na	2.31
		O	58.02
Total	100%	Total	100%

4. Conclusion

LSCF/YSZ-SDC and LSCF/YSZ-SDCC with different composition of YSZ composites (50:50, 60:40 and 70:30) wt.% were studied through their phase stability and compatibility. For the preliminary stage, all LSCF/YSZ-SDC and LSCF/YSZ-SDCC dual composites powder are compatible and ready to proceed to the next step which is the fabrication of the symmetrical cells. The overall performance for different compositions will be studied further during the preparation of the symmetrical cells and another cell performance testing as to ultimately find out the best ratio composition in this study.

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