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Fabrication and Characterisation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-SDC Composite Cathode

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Abstract. Composite cathode is a promising material to be used as electrodes in fuel cells. The fabricated composite cathode materials in this study are comprised of a mixture of submicron $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF6428) powders with two types of nanoscale ionically conducting ceramic electrolyte materials, samarium-doped ceria (SDC) and SDC-carbonate (SDCc). 30 – 50 wt% of electrolyte materials are added to the LSCF6428 cathode via the solid state method. The composite powders were ball-milled in ethanol and calcined at the temperature range of 800°C to 900°C for 2 hours in air. The composite cathode powders are characterised in terms of morphology and crystal structure. It is found that after calcining, the LSCF and the electrolyte materials retained their original structures as there was no chemical reaction between the two components. In addition, the LSCF-SDC composite cathode powders were found to exhibit a narrower distribution in size compared to the LSCF-SDC carbonate powders.

Introduction

Recently, most research in solid oxide fuel cells (SOFCs) are devoted to the development of intermediate to low temperature (500-700°C) SOFCs. Lowering the operating temperature of SOFCs is necessary to reduce the degradation of the electrodes and electrolytes and to improve the material compatibility. However, the reduction of the operating temperature of the SOFCs also increases the electrolyte resistance and inefficiency of the electrode materials. Two current practices that have been found to be potentially able to solve the above problems are (1) reducing the thickness of the electrolyte which will reduce the electrolyte resistance and (2) designing a high performance electrode with a low polarisation resistance such as using a composite cathode. The latter practice appears as a promising way to attain better performance of SOFCs at lower operation temperatures [1,2,3].

The replacement of conventional cathode materials, lanthanum strontium manganite (LSM) with mixed ionic-electronic conducting ceramic electrode materials such as lanthanum strontium cobalt ferrite (LSCF) was the first approach that has been done to obtain a higher performance of cathodes. The second approach involves the addition of electrolyte with the cathode materials which are then called composite cathodes. Composite technology allows the creation of electrodes with higher effective surface area to increase the efficiency of the exchange reactions, and, consequently, to decrease the electrode over potentials [4].

Recently, lanthanum strontium cobalt ferrite (LSCF) has been considered to be one of the most highly potential cathode materials for intermediate to low temperature SOFCs. Since perovskite LSCF is a mixed oxygen ionic and electronic conducting material, it offers excellent over potential

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and electrical conductivity at lower temperatures [5,6,7]. The combination of LSCF with ionic conducting materials especially with ceria-based electrolytes result in extending the electrochemical activation area due to the higher ionic conductivity of these electrolytes compared to perovskite. The performance of the LSCF composite cathode is significantly dependent on the sintering temperature, microstructure and composition [8,9,10,11]. Therefore, the influences of those parameters need to be closely monitored for the new developed composite cathode materials.

In the present study, the LSCF-based composite cathodes were made from commercial LSCF6428 and SDC electrolyte powders. Meanwhile, the in-house developed SDC-carbonate powders were employed to produce LSCF-SDCc composite powders. The relationship between calcining temperature, composition and properties of the composite cathode were investigated.

Methodology

The preparation of the SDC carbonate (SDCc) powder was conducted via solid state method. The 80wt% of SDC nanopowder (Sigma Aldrich Sdn. Bhd. Selangor, Malaysia) was mixed with 20wt% carbonates (67 mol% Li_2CO_3: 33 mol% Na_2CO_3) [12]. The mixture was heat treated at 680°C for 1 hour.

The LSCF-SDC composite cathode powders were prepared from a mixture of commercial lanthanum strontium cobalt ferrite (LSCF6428, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) powder of particle size 0.3-0.6 µm and nanopowder samarium-doped cerium oxide (SDC, $Sm_{0.15}Ce_{0.85}O_{1.95}$) from Sigma Aldrich Sdn.Bhd.. Meanwhile, the LSCF-SDC carbonate (LSCF-SDCc) composite employed the combination of the in-house developed SDCc (20 wt% Na/Li carbonate in SDC) powder with the commercial LSCF6428 powder. Both the LSCF composite powders were ball-milled in ethanol for 2 hours followed by overnight drying in an oven at 60°C. The dried composite cathode powders were ground in an agate mortar and then calcined at a temperature range of 800-900°C for 2 hours in air. The LSCF-SDC and LSCF-SDCc composite powders had compositions varying from 50 to 70 wt% LSCF6428, and henceforth named as LSCF-SDC55 (or LSCF-SDCc55) to LSCF-SDC73 (or LSCF-SDCc73) respectively. Table 1 shows the composition of the composite cathode powders and the calcination temperature investigated.

Table 1. Composition of the composite cathode powders and calcination temperatures

Composite powder	LSCF6428 (wt%)	SDC (wt%)	SDCc (wt%)	Calcination temperature (°C)
LSCF-SDC55	50	50	-	Each of the composite powders were calcined at 800, 850 and 900°C
LSCF-SDC64	60	40	-	
LSCF-SDC73	70	30	-	
LSCF-SDCc55	50	-	50	
LSCF-SDCc64	60	-	40	
LSCF-SDCc73	70	-	30	

The powder preparation process was followed by its characterisation. The confirmation of phase and structure of the prepared composite powders were made using X-ray diffraction (XRD) (Bruker D8 Advanced diffractometer) at Cu Kα radiation, λ = 0.15406nm. The selected 2θ range was from 20° to 80° scanning at a step of 0.02°. The particle size of the composite powders was determined by using a laser particle analyser (Zetasizer Nanoseries ZS, Malvern). Surface area analysis was conducted on the composite powders using BET surface area analyzer (Altamira Instruments AMI-200). Additionally, a Zeiss Supra 55VP Field Emission Scanning Electron Microscope (FESEM) was employed to analyse the morphology of the calcined composite powders.

Results and Discussion

Fig. 1 shows the X-ray spectra of the pure LSCF6428 and the electrolyte SDC. The commercial powder LSCF6428 and SDC has the phase of rhombohedral pervoskite and cubic respectively [13,14]. The XRD patterns of the composite cathodes LSFC-SDC55 calcined at different temperature are also illustrated in the same figure. The resultant LSCF-SDC55 composite powders were able to maintain their own structures after calcination and no major second phases were observed. Furthermore, the XRD outcomes of the LSCF-SDCc (LSCF-SDCcarbonate) composite powders which can be referred to in Fig. 2 show good agreement with the analysis of the results for the LSCF-SDC composite powders. The molten carbonate in SDCc electrolyte powder exist as an amorphous phase and does not influence the phase of the pure SDC [12,15]. This demonstrated that there was no chemical reaction between the two components as no major second phases was observed [14].

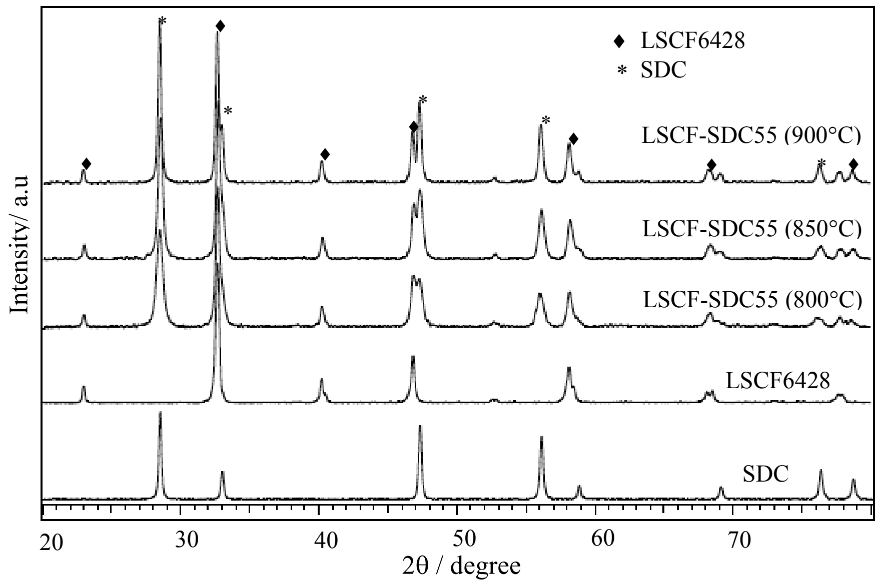

Fig 1. XRD patterns of the SDC, LSCF6428 powders and the calcined (800, 850 and 900°C) LSCF-SDC55 composite cathodes

The other LSCF-SDC and LSCF-SDCc composite powders with different compositions and calcination temperatures also depicted similar outlines as the LSCF-SDC55 composite powders. This can be seen in Fig. 3 which illustrates the X-ray pattern of various LSCF composite powders calcined at 900°C. It may be concluded therefore, that it is possible to get high performance cathode since each component in the composite cathode was able to maintain its own function such as enhancing the cathode reactions and reducing the polarisation between the electrode and the electrolyte.

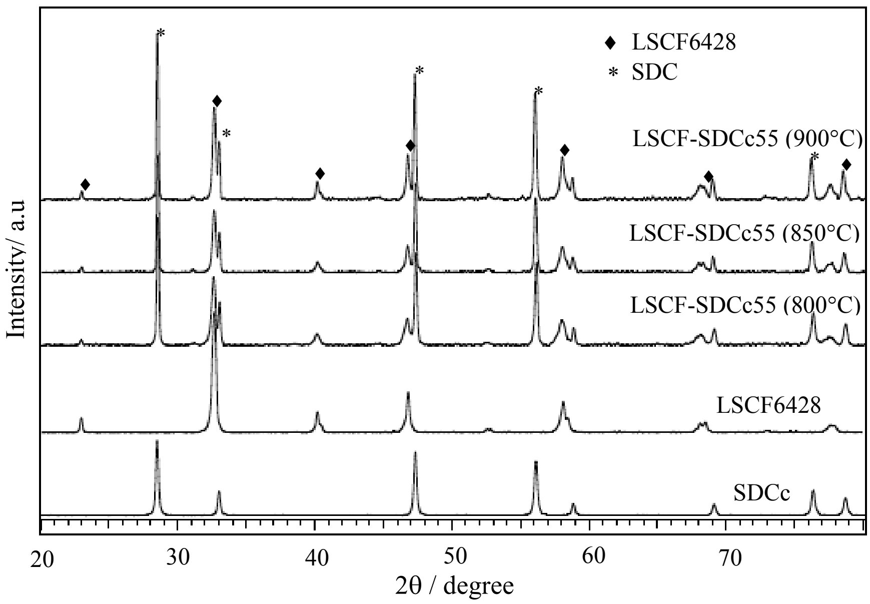

Fig 2. XRD patterns of the SDCc, LSCF6428 powders and the calcined (800, 850 and 900°C) LSCF-SDCc55 composite cathodes

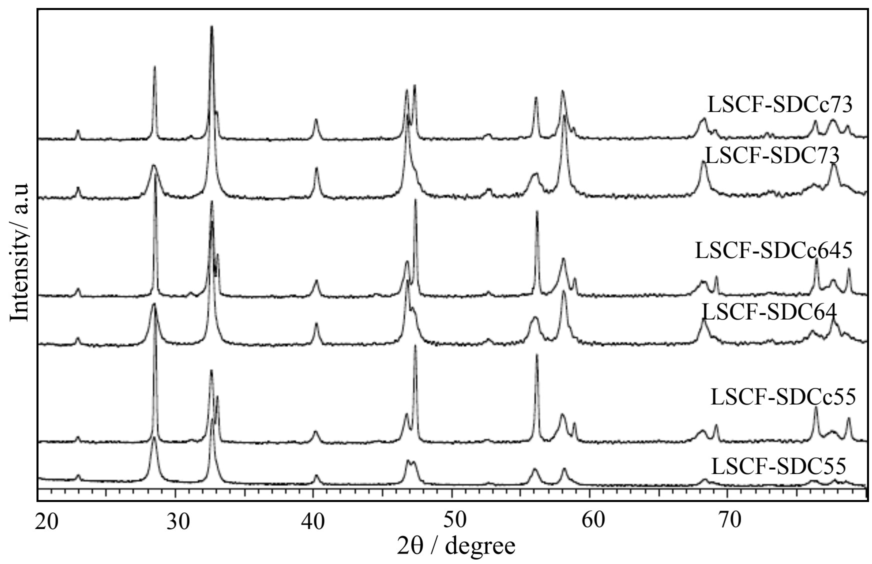

Fig 3. XRD patterns of the LSCF composite cathode powders calcined at 800°C

The particle size of the composite cathode powders was determined using laser Doppler velocimetry and phase analysis light scattering. The increment of particle size of the both types of the composite powders was observed upon the increment of the calcination temperature. This phenomena is due to the growth of the particles, as similarly reported by Seabaugh & Swartz [4]. The LSCF-SDC composite powders that were calcined between 800-900°C exhibited particles in the size range of 0.4-0.5 µm with surface area between 6-13 m^2/g. The surface area of the particles offers a guide in choosing the appropriate method for fabrication of the cathode. In the present work, the obtained surface areas of the prepared composite cathodes are suitable for screen printing process. In addition, the calcination temperatures, the starting sizes and surface areas of the composite cathode particles have been identified to give an influence to the electrode performance [4]. A wider distribution in particle size was obtained for the LSCF-SDCc composite powders at 0.4-1.0 µm with bigger surface area (3-1 m^2/g). With reference to Jarot et al. [12] and Bodén et al. [16], the increment in the particle size of the LSCF-SDCc composite powders compared to the LSCF-SDC composite was mostly due to the coating of the $(Li/Na)_2CO_3$ amorphous phase over the electrolyte and electrode particles.

Fig. 4(a)-(d) show the microstructure of the composite cathode powders calcined at 850°C for 2 hrs. In agreement with the particle size analysis and as can be seen in the SEM micrographs, the LSCF-SDCc composite cathode powders were found to have larger particle sizes compared to the LSCF-SDC powders. The morphology of the composite cathode powders supported the argument that molten carbonate from the SDCc electrolyte surrounded the LSCF-SDCc composite cathode particles and contributed to the increase in particle size.

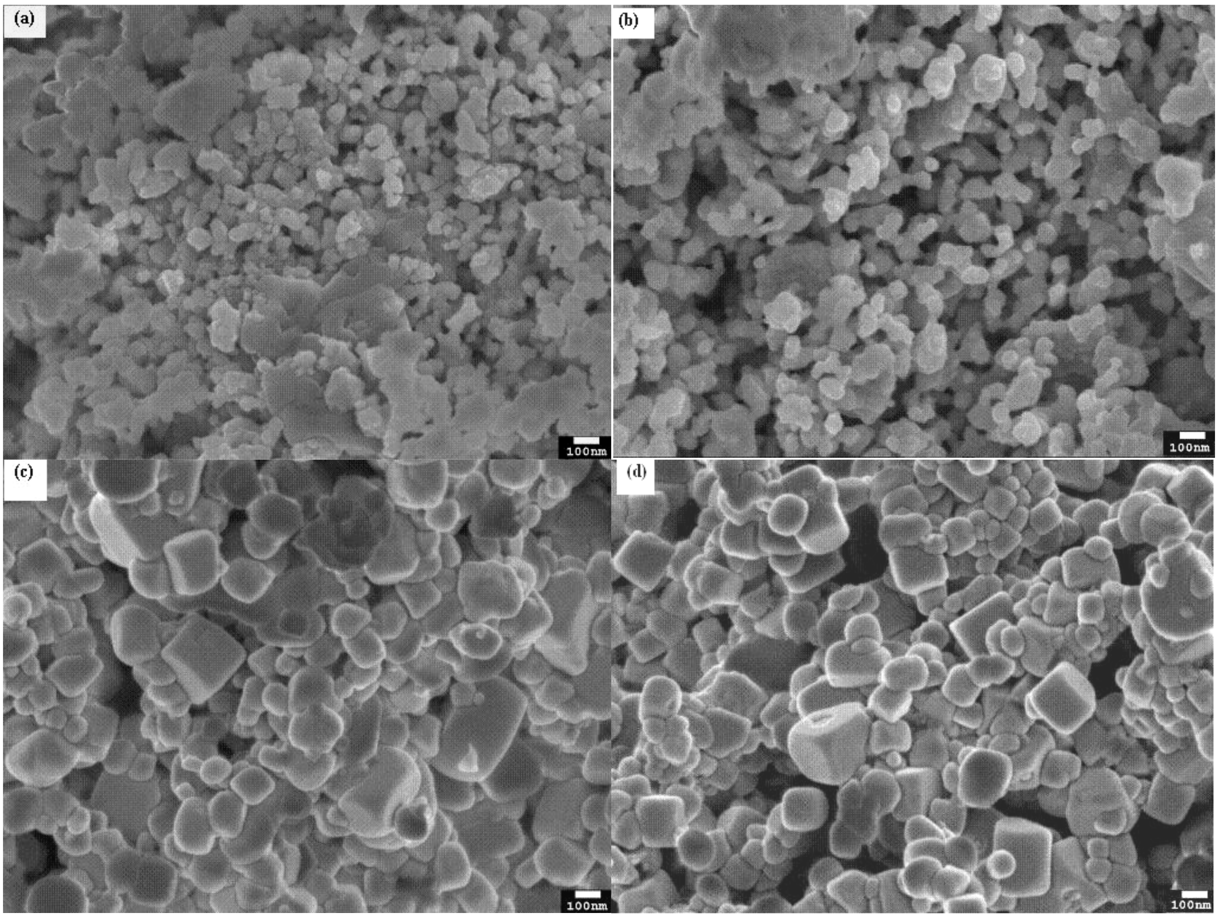

Fig 4. The SEM micrographs of the LSCF-SDC composite powders (a) LSCF-SDC64, (b) LSCF-SDC73 and LSCF-SDC carbonate composite powders (c) LSCF-SDCc64, (d) LSCF-SDCc73 calcined at 850°C

Summary

The mixing of electrode powder with a nanoscale electrolyte has been accomplished by a simple milling technique for the preparation of the LSCF6428 composite cathode powders. The obtained composite powders were calcined at different temperature and characterised in order to study their properties as cathode material for the SOFCs. The addition of 30-50 wt% of electrolyte powders into the LSCF6428 followed by calcining at temperature between 800-900°C showed good compatibility as no secondary phases or chemical reaction were produced. The findings in this work can be a preliminary indication for these composite powders to be used as cathode component of SOFCs. Further investigation is expected to explore on other characteristics such as thermal properties, electrochemical properties and electrical conductivity of these composite cathodes.

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