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CHARACTERIZATION OF $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ CATHODE POWDERS PREPARED VIA ACTIVATED CARBON-ASSISTED SOL-GEL METHOD

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ABSTRACT

In this study, the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode powders were prepared by an activated carbon-assisted sol-gel method. The activated carbon was used as a dispersing agent to produce well-dispersed particle and improve the microstructure of the cathode powders. The powders were calcined in air at the temperature range of 400 to 1100 ^oC. The characterizations of the resultant powders were performed by using X-ray diffractometer (XRD), field emission-scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET) analysis and impedance spectroscopy. Single perovskite phase of LSCF was completely formed at 700 ^oC and preserved even after calcination temperature of 1100 ^oC. As confirmed by BET analysis, a higher surface area was obtained for powder sample prepared with the aid of the dispersing agent, which is 11.02 m^2g^{-1} . The FESEM images confirm a good contact of the cathode and electrolyte layer. The electrochemical measurement of LSCF symmetrical cell at 750 ^{o} was performed and evaluated. The impedance spectra obtained were resolved by a fitting procedure using an equivalent circuit that consists of a combination of four parallel pairs of resistor-constant phase element (R-CPE) in series. The different impedance arc were allocated to the corresponding processes using the capacitance (C) value related to each arc. Grain boundary response, interfacial processes and cathode reactions were respectively assigned by their associated capacitance value which is $C \approx 10^{-10}$, $C \approx 10^{-7}$, and $C \approx 10^{-3}$ F.

Keywords: SOFC; cathode material; LSCF; electrochemical study;

INTRODUCTION

Solid oxide fuel cells (SOFCs) are an emerging technology for stationary power production as it offers an environmentally friendly alternative in generating electricity. The high operating temperatures (800-1000 ^oC) of the conventional SOFCs significantly limits the choice of the fabrication materials and encourage cell degradation. Reduction of operating temperature to an intermediate temperature range (400-750 ^oC) is feasible in that low operating temperatures has the following advantages: (1) Utilization of

inexpensive component materials, (2) rapid startup and shutdown and (3) reduce cell degradation [1]. While improvements in IT-SOFC have been achieved, their performance is still typically limited by high cathode polarization resistance. The reduction in the operating temperature has led to a significance decrease in the cathode activity [2, 3]. Accordingly, the conventional SOFC cathode, strontium doped lanthanum manganite (LSM), is not suitable for IT-SOFC operation due to its low activity below 800 ^{o}C. Therefore, the development of high-quality cathode material is critical for further improvement of the fuel cell performance. The performance of the cathode depends not only on the material, but also very much on its structure, which can be controlled during the fabrication process.

In this study, lanthanum strontium cobalt ferrite oxide (LSCF) cathode powders are prepared by a sol-gel method utilizing two different types of chelants namely ethylene diamine tetraacetic acid (EDTA) and citric acid. In addition, activated carbon is also added during the synthesizing process as a dispersing agent in an attempt to control the distribution and particle size of the cathode powders. The control of cathode microstructure is important as the small particle size and high surface area are favored for the improvement of the cathode activity. The LSCF powders synthesized with the assistance of the activated carbon as a dispersing agent are characterized for morphology, structural and electrochemical properties. The evaluation of LSCF cathode is investigated against a proton conducting electrolyte, $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) and its electrochemical performance is reported.

EXPERIMENTAL

BCZY powders were synthesized by a combined citrate-EDTA complexing sol-gel process [4]. The synthesis of LSCF is described as follows. The stoichiometric composition of $La(NO_3)_3.6H_2O$ (99.9%, ACROS), $Sr(NO_3)_2$ (99%, ACROS) , $Co(NO_3)_2.6H_2O$ (99%, ACROS) and $Fe(NO_3)_3.9H_2O$ (99%, ACROS) were first dissolved in 100 ml of deionized water. Citric acid monohydrate (CA) (99.5%, MERCK) was added into the solution, followed by ethylene diamine tetra-acetic acid (EDTA) (99%, ACROS) powder. The solution was subsequently heated in 70 ^{o}C water bath under continuous stirring. The molar ratio of CA and EDTA added to the mixture solution with respect to the overall metal cations content was 2:1:1 (CA:EDTA:Metal cation). 5 grams of charcoal activated carbon (HmbG) was then added as a dispersing agent to promote dispersion and prevent clumping of the particles. Under stirring and heating, a black viscous gel was obtained, which was solidified by pre-heating at 100 ^{o}C for 12 h and finally calcined at 700 ^{o}C for 5 h to obtain a pure phase of LSCF. Phase formation of the oxide compound was verified by X-ray diffraction (XRD) (PANalytical X'Pert PRO MRD PW3040), employing Cu K_{α} radiation from 20^{o} to 80^{o} in the step of 0.05^{o} at 2θ. Field emission scanning electron microscopy (FESEM) (Carl Zeiss SMT Supra 40VP) was employed to observe the microstructures of the LSCF powders. The micrographs obtained were used to estimate the particle size and the morphology of the sample using an image analysis system (ImageJ 1.45p). The specific surface area of the LSCF powder was determined using BET analyzer (Quantachrome

Autosorb AS1C).

Symmetrical cells with the configuration of LSCF|BCZY|LSCF were used for the electrochemical impedance studies. Dense BCZY pellets of 11 mm in diameter and 0.9 mm in thickness were obtained after sintering in air at 1450 ^{o}C for 12 h. To prepare the electrode, the LSCF powders, Polyvinyl Pyrolidone (PVP) and ethanol were mixed to form cathode slurry. The slurry was then painted onto the BCZY surface using an in-house rolling technique, followed by firing at 950 ^{o}C for 2 h. Measurement of the electrochemical impedance characteristic was conducted at open circuit voltage (OCV) in ambient air over a temperature range of 500-800 ^{o}C. The frequency range of 10 mHz to 1 MHz with an AC signal amplitude of 100 mV was applied using a ZIVE SP2 Electrochemical Workstation. ZMAN™ 2.2 f3 (ZIVE LAB) software was used to analyze the impedance arcs referred to the equivalent circuits of four parallel pairs of R-CPE in series.

RESULTS AND DISCUSSION

XRD analysis

Figure 1 shows X-ray diffraction pattern of LSCF powders calcined between 400 and 1100 ^{o}C. The profiles presented characteristic peaks of the perovskite LSCF phase appears after calcination process at 500 ^{o}C together with small amount of secondary phase at $2\theta \approx 26.5^{o}$ and 44^{o} which correspond to the presence of La_2O_3 and Co_2O_3. The complete formation of a single perovskite LSCF phase with orthorhombic structure is achieved at 700 ^{o}C (JCPDS 89-1268). In addition, the purity of the LSCF phase was preserved even after thermal treatment at 1100 ^{o}C, signifying that the compound remains stable even at elevated temperatures.

The chemical compatibility between the electrolyte and cathode is also worth being evaluated as the interfacial reaction between the electrolyte and cathode easily generates less conductive phases, which would lead to significant increase of polarization resistance and ohmic resistance of the cell [5]. In order to get clear information about the compatibility and possible phase reaction at the cathode-electrolyte interface layer during the high-temperature firing, the solid state reaction between LSCF and BCZY were investigated by mixed powders. Figure 2 shows the X-ray diffraction patterns of LSCF, BCZY and the LSCF+BCZY mixture after the heat treatment process. As can be seen from the figure, no additional secondary phase appears even after fired at 1000 ^{o}C, and only peaks corresponding to LSCF and BCZY can be found in XRD patterns, revealing good chemical compatibility between the cathode and electrolyte under the condition studied.

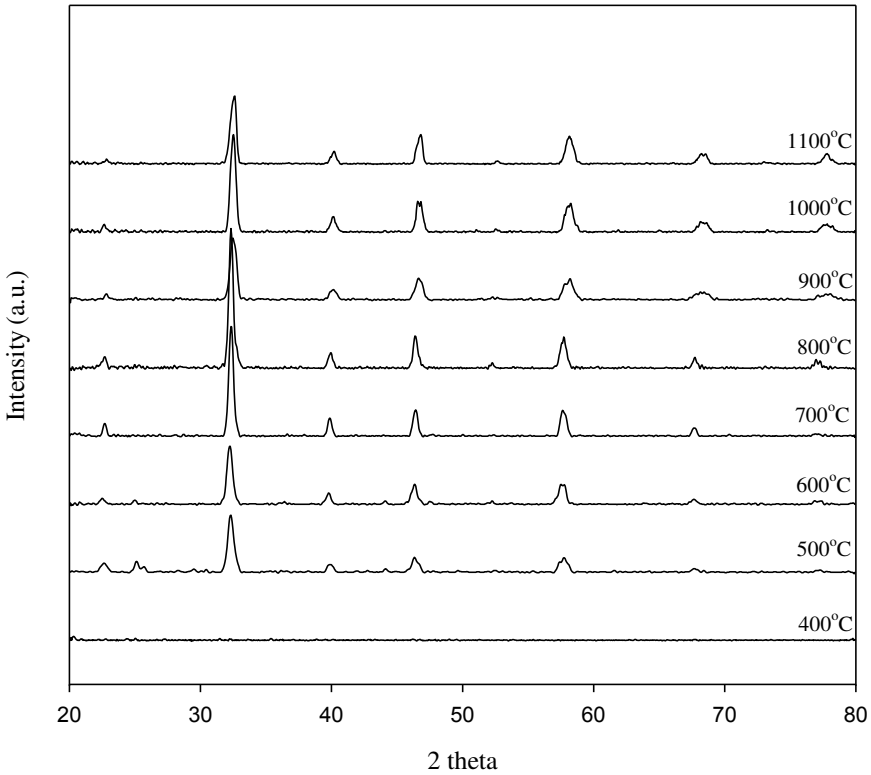

Figure 1: X-ray diffraction pattern of LSCF powders after calcined at temperature ranging from 400 to 1100 °C

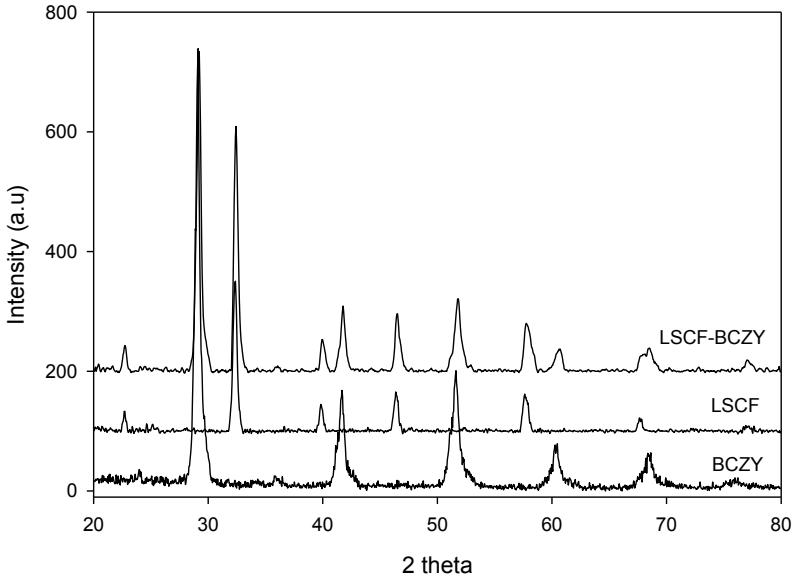

Figure 2: X-ray diffraction patterns of LSCF, BCZY and the LSCF-BCZY mixture after heat treatment at 1000 °C

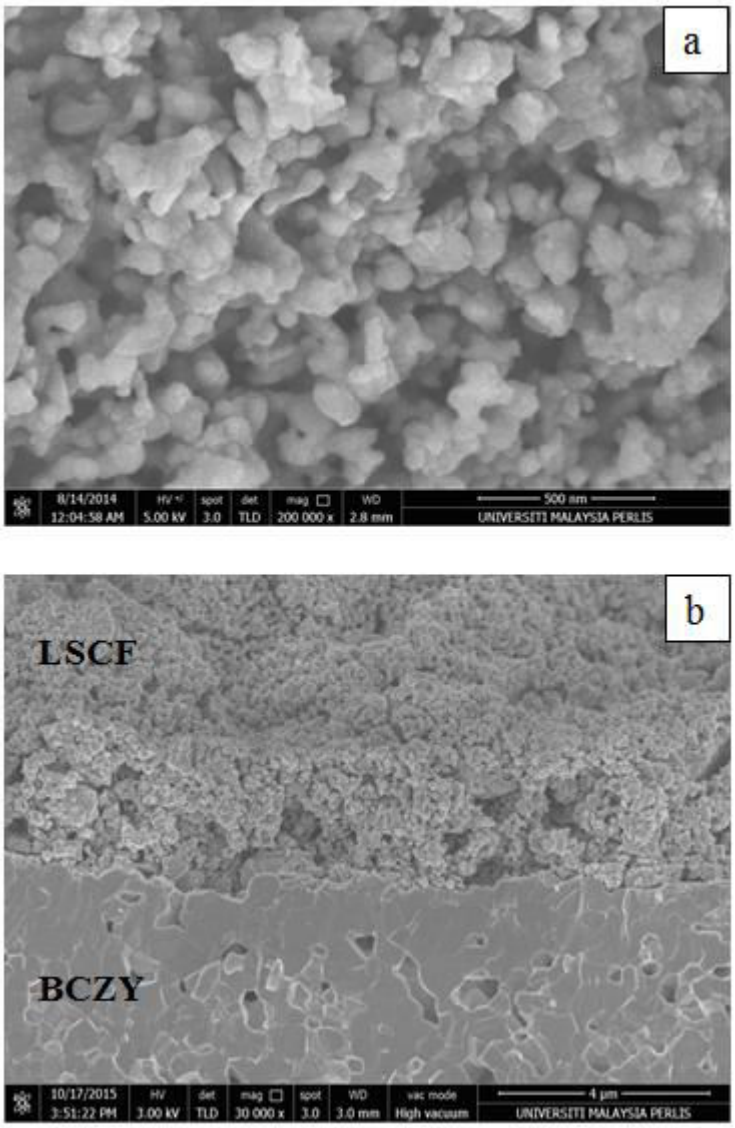

Figure 3: FESEM images of a) top view surface micrograph of the LSCF cathode on BCZY electrolyte sintered at 950 ^{o}C for 2 h, b) cross-section view at the LSCF|BCZY interface

Microstructure characteristic

The microstructure of the sintered cathodes is one of the most important factors governing the electrochemical performance of the cell. Therefore, keeping the calcination temperature as low as possible is favorable in microstructural preservation as high calcination temperature always results in coarser particles which reduce the active surface area for reaction. As discussed in the previous part, a single phase of LSCF cathode material was attained at a calcination temperature of 700 ^{o}C. At this temperature, BET analysis depicts that the surface area of the sample is 11.02 m^2g^{-1}. The surface area obtained is comparatively higher than those reported in the previous

works [1, 6]. Figure 3a shows the surface micrograph of the LSCF cathode on BCZY electrolyte sintered at 950 ^{o}C for 2 h. It seems that the grains are well connected with each other after sintering with the average grain size of about 70 nm in diameter. The cathode obtained displays a fine uniform microstructure with appropriate porosity. A cathode having more porosity (20 to 40 %) and smaller particles will allow better oxygen diffusion through the cathode, resulting in better electrochemical kinetics. Figure 3b shows the FESEM image of a cross-section at the LSCF|BCZY interface. The thickness of the cathode layer is about 10 µm. As can be observed, LSCF cathode exhibits good, continuous contact with dense BCZY substrate without any obvious delamination and cracks. The good adhesion of these two layers ensures a low contacting resistance between cathode and electrolyte layers [7].

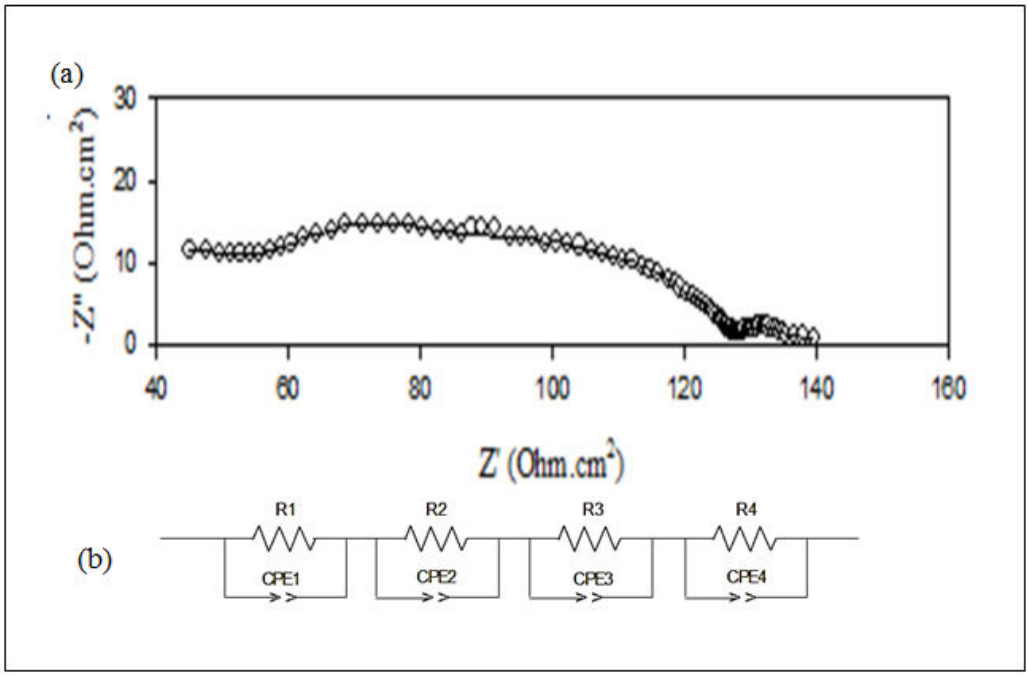

Figure 4: (a) Impedance spectrum of LSCF|BCZY|LSCF symmetrical cell at 750 ^{o}C in air. Dots are the experimental data and solid lines the fit using (R1Q1)(R2Q2)(R3Q3)(R4Q4) circuit, (b) equivalent circuit to represents the sample's responses

Electrochemical impedance measurement

Figure 4 is an impedance spectrum of LSCF|BCZY|LSCF symmetrical cell recorded at 750 ^{o}C in air. The spectrum was fitted using the equivalent circuit (R1Q1)(R2Q2)(R3Q3)(R4Q4), as shown in Figure4b. In the circuit, R and Q denote for resistance and constant phase element (CPE), respectively. Four impedance arcs that correspond to the four responses were identified based on the value of the pseudo capacitance (C) associated to each arc. The first arc at higher frequency (R1-Q1) could be assigned to the contribution of the BCZY electrolyte which is considered for grain boundary response ($C \approx 10^{-10}$ F). For the middle and low frequency contribution, R2-Q2

($C \approx 10^{-7}$ F) and R3-Q3 ($C \approx 10^{-7}$ F) circuits is probably associated with charge-transfer processes, which include oxygen ion diffusion in the cathode bulk and incorporation of oxygen ions from three-phase boundaries [8]. The low frequency arc, R4-Q4 (associated with a high capacitance value $C \approx 10^{-3}$ F) can be attributed to diffusion processes, which include oxygen adsorption-desorption and surface diffusion of intermediate oxygen process. This low-frequency arc only appears at the temperature above 600 ^{o}C and lower partial pressure of oxygen (0.2 atm) as reported in other works published elsewhere [1, 9].

CONCLUSION

LSCF powders have been synthesized by application of activated carbon as a dispersing agent. Reduction of agglomerated particles by the implementation of this type of dispersing agent is achieved in which higher surface area was obtained as confirmed by the BET analysis. The improved microstructure increases the potential of LSCF cathode to be applied as one of the high-quality cathode material for IT-SOFC application. Four impedance responses were obtained from EIS measurement where each allocated to grain boundary response, interfacial processes and cathode reactions. The capacitance values of the respective process were each assigned at $C \approx 10^{-10}$ F, $C \approx 10^{-7}$ F and $C \approx 10^{-3}$ F.

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