

Evaluation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ as a Potential Cathode for Proton-Conducting Solid Oxide Fuel Cell

(Penilaian $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ sebagai Potensi Katod untuk Sel Fuel Oksida Pepejal Pengkonduksi Proton)

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ABSTRACT

The application of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) as a potential cathode working on a $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) electrolyte for proton conducting solid oxide fuel cell was investigated. LSCF nanoceramic powders were synthesized by an activated carbon-assisted sol-gel process using metal nitrate-based chemicals. The LSCF powder was transformed to a slurry and spin-coated onto both surfaces of BCZY pellet to form a symmetrical cell with the configuration of LSCF|BCZY|LSCF. The symmetrical cell was subsequently sintered at 950°C for 2 h to allow a good contact formation between electrode/electrolyte layers. The phase structural verification of the calcined powders was investigated by X-Ray diffractometer (XRD). Field-emission scanning electron microscopy (FESEM) was employed to examine the morphology of the sintered cell. The electrochemical behaviour of the symmetrical cell was studied by an electrochemical impedance spectroscopy. The formation of a single perovskite LSCF phase with a crystallite size of 20 nm was obtained at 700°C as corroborated by XRD analysis. The FESEM images showed a good contact between LSCF cathode and BCZY electrolyte at electrode/electrolyte interfacial layer. The ASR obtained for LSCF symmetrical cell measured at 700°C with and without Pt current collector is 0.87 and 31.25 Ωcm^2 , respectively.

Keywords: Cathode material; morphology; proton-conducting solid oxide fuel cell

ABSTRAK

Kajian penggunaan $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) sebagai potensi katod ke atas elektrolit $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) untuk sel fuel oksida pepejal pengkonduksi proton telah dijalankan dalam penyelidikan ini. Serbuk nano seramik LSCF disintesis melalui kaedah sol-gel menggunakan bahan kimia berasaskan garam nitrat dibantu dengan serbuk karbon teraktif sebagai agen penyerakan partikel. Serbuk LSCF yang terhasil dijadikan sebagai dakwat katod dan disalutkan di atas permukaan pelet elektrolit dengan menggunakan teknik 'spin-coat' untuk menghasilkan sel simetri dengan konfigurasi LSCF|BCZY|LSCF. Sel simetri tersebut seterusnya disinter pada suhu 950°C untuk menghasilkan sentuhan yang baik di lapisan antaramuka elektrod/elektrolit. Pengesahan struktur fasa serbuk yang dikalsinkan telah dikaji dengan menggunakan difraktometer sinar-X (XRD). Mikroskop imbasan elektron (FESEM) digunakan bagi mengkaji morfologi sel simetri yang telah disinter. Kajian sifat elektrokimia sel simetri dijalankan dengan menggunakan spektroskopi impedans. Analisis XRD menunjukkan bahawa pembentukan fasa perovskit tunggal LSCF dengan saiz kristalit 20 nm telah diperolehi pada suhu 700°C. Imej FESEM mempamerkan sentuhan yang baik di antara lapisan katod LSCF dengan elektrolit BCZY di bahagian antaramuka elektrod/elektrolit. Rintangan luas permukaan yang didapati hasil pengukuran sel simetri LSCF pada suhu 700°C dengan dan tanpa kehadiran Pt sebagai pengumpul arus masing-masing adalah 0.87 dan 31.25 Ωcm^2 .

Kata kunci: Bahan katod; morfologi; sel fuel oksida pepejal pengkonduksi proton

INTRODUCTION

Solid oxide fuel cells (SOFCs) are energy generator devices which effectively convert chemical energy into electrical energy. It has appeared as an emerging technology for future power generation due to the increasing demand for clean and renewable energy sources. The operation of conventional SOFCs is based on the oxygen ion-conducting oxides electrolytes. Currently, there is considerable interest in proton-conducting oxides electrolytes for the SOFCs application. The proton-conducting SOFCs or also known as proton-conducting

fuel cells (PCFCs) exhibit more advantages as compared to the typical SOFCs based on oxygen-ion-conducting electrolyte as it displays lower activation energy and high energy efficiency at an intermediate temperature of 500-800°C (Yang et al. 2012). Moreover, the application of proton-conducting electrolyte prevents the fuel dilution since water generation takes place at the cathode side of the cell. Among the materials applied for PCFCs electrolyte, $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) is one of the most popular proton conductors which have been demonstrated to exhibit adequate proton conductivity as well as sufficient chemical and mechanical stabilities.

To that end, the development of appropriate cathode materials for PCFCs application is still fresh and most of the cathode materials currently employed in PCFCs are just generally reassigned from SOFCs cathodes. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) is one of the mixed ionic-electronic conductors (MIEC) adapted from SOFCs application which has been considered as a promising cathode material for PCFCs due to its high ionic and electronic conductivity as well as excellent catalytic activity (Baharuddin et al. 2014; Jiang 2002). Extensive efforts devoted to developing the suitable cathode materials for PCFCs generally focused on the cathode composition and optimization of the cathode microstructure. Even though the intrinsic properties of a cathode material are important in enhancing the cathode performance of PCFCs, the actual cathode performance is also highly influenced by the material preparation and electrode microstructure. A small particle size and high surface area of cathode particles are favored for PCFCs cathode in enhancing the catalytic performance of the electrode (Kim et al. 2011; Zhou et al. 2006). Therefore, it is importance to control the cathode microstructure so that the triple phase boundary (TPB) region which defines the active reaction sites could be established as broad as possible.

In this study, LSCF cathode powders are prepared by a sol-gel method using ethylene diamine tetra-acetic acid and citric acid as chelates assisted with the addition of activated carbon as the dispersing agent. The dispersing agent is used as the synthesizing aid to control the microstructure by producing a well-dispersed and less agglomerated cathode particle. The cathode materials prepared were physically and electrochemically characterized and evaluated for possible application in PCFCs.

MATERIALS AND METHODS

SAMPLE PREPARATION

The synthesis of LSCF is described as follows. The stoichiometric composition of lanthanum nitrate (99.9% purity), strontium nitrate (99% purity), cobalt nitrate (99% purity) and ferric nitrate (99% purity) were dissolved in 100 mL of deionized water. Citric acid monohydrate (CA) (99.5% purity) was introduced into the solution, followed by addition of ethylene diamine tetra-acetic acid (EDTA) (99% purity) powder. The solution was subsequently heated in 70°C water bath under continuous stirring. 0.4 mol of charcoal activated carbon was then added as a dispersing agent to promote dispersion and prevent clumping of the particles. Under continuous stirring and heating process, a black viscous gel was obtained. Next, the gel was solidified by pre-heating at 100°C for 12 h and finally calcined at 700°C for 5 h to obtain a pure perovskite phase of LSCF.

For the electrochemical impedance measurement, an electrolyte supported half-cell of LSCF|BCZY|LSCF was fabricated. Prior to the cell fabrication, BCZY powders was synthesized by a combined citrate-EDTA complexation sol-gel process (Abdullah et al. 2012) and pressed into a

pellet and sintered at 1500°C for 10 h in air. LSCF powders, polyvinyl pyrrolidone (PVP) and ethanol were then mixed to form cathode slurry. The slurry was spin-coated on BCZY surface to form the required cell followed by firing at 950°C for 2 h.

SAMPLE CHARACTERIZATION

Phase formation of the perovskite compound was verified by X-ray diffraction (XRD) analysis, employing Cu-K α radiation from 20° to 80° in step of 0.05° at 2 θ . From the XRD results, the average crystallite size, D , was estimated based on the Scherrer formula as in (1).

$$D = 0.9\lambda/(\beta \cos \theta), \quad (1)$$

where λ refers to the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM) and θ denotes the Bragg angle. The XRD density, of the sample was calculated using (2) (Galasso 1969).

$$\rho = \frac{nA}{V_c N_A}, \quad (2)$$

where n is the number of atoms associated with each unit cell; A is the atomic weight; V_c is the volume of the unit cell; and N_A is the Avogadro's number. The lattice parameter of the LSCF samples was estimated based on Bragg's Law using Mathcad 14 software. Field emission scanning electron microscopy (FESEM) was employed to observe the morphology of the LSCF|BCZY interfacial region. The micrographs obtained was used to estimate the cathode surface porosity using imageJ software. The electrochemical impedance measurement was conducted at open circuit voltage (OCV) in ambient air at 700°C. The frequency range of 10 mHz to 1 MHz with an AC signal amplitude of 100 mV was applied using an electrochemical impedance spectroscopy (EIS). Prior to the EIS measurement, the cell was stabilized at 700°C for 24 h to achieve the equilibrium condition. The impedance spectra obtained were analyzed using the ZMAN software. The capacitance value for each impedance response was calculated using (3).

$$C = \frac{1}{Y^n} \times R^{\left(\frac{1}{n}-1\right)}, \quad (3)$$

where R denotes the resistance while Y and n refers to the parameters associated with the constant phase element (CPE).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the as prepared and LSCF powders after calcined at 700°C are shown in Figure 1. The calcined powders have well crystalline perovskite phase of LSCF and the diffraction peaks can be indexed to (110), (020), (202), (220), (132), (224), (332). All the diffraction peaks can be assigned to single-phase of LSCF with orthorhombic structure (JCPDS 89-1268). In addition, the lattice parameters values estimated are close to the values obtained for the JCPDS card for LSCF compound ($a = 5.4750 \text{ \AA}$; $b = 5.5360 \text{ \AA}$; $c = 7.7691 \text{ \AA}$).

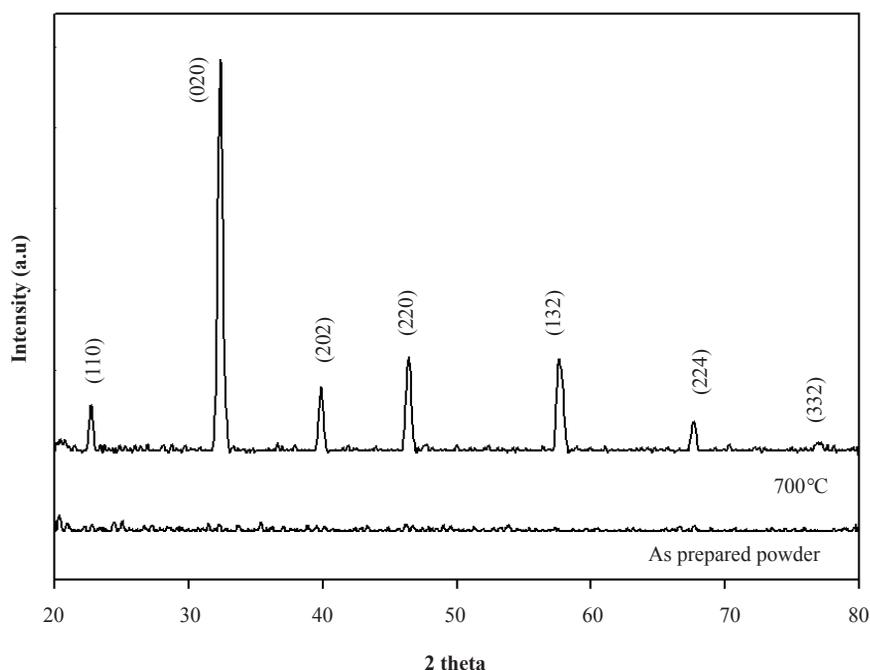


FIGURE 1. XRD spectra of the as prepared LSCF powder and powder calcined at 700°

The phase structure of the LSCF sample synthesized with the aid of activated carbon is similar with the pristine sample prepared in our previous study (Ismail et al. 2016), signifying that the phase formation of LSCF is not affected by the addition of activated carbon. The XRD density and crystallite size calculated for the sample calcined at 700°C is 6.32 g cm⁻³ and 20 nm, respectively. The formation of single phase attained in this study is relatively at a lower temperature compared with the temperature over 900°C prepared by combustion and other synthesis methods (Baqué et al. 2008; Chanquia et al. 2014). Additionally, the phase structure of the LSCF remains unchanged even after calcined at 1100°C, suggesting the stability of the compound at elevated temperature.

The application of activated carbon during the synthesizing process produced well-dispersed cathode particles with fewer agglomerates thus favored the cell fabrication process by providing better cathode microstructure. Figure 2 shows the micrographs of the surface and fractured pellet cross-section at the interfacial region of LSCF|BCZY. The cathode surface shows a fine uniform microstructure with moderate porosity (30%) and well-connected grains. Appropriate porosity (20-40%) will allow better oxygen diffusion through the cathode while the good connections between the particles will significantly decrease the resistance of bulk/surface diffusion of oxygen species. It can be observed that the prepared cathode shows a good interfacial contact with BCZY electrolyte with no signs of delamination. The good adhesion of these two layers is important as it ensures a low contacting resistance between the cathode and electrolyte layers (Sun et al. 2011).

Figure 3 presents the impedance spectra recorded on the LSCF|BCZY|LSCF cell with and without Platinum

(Pt) current collector at 700°C in air. As shown in Figure 3, the resistance of the cells measured with Pt current collector was remarkably lower than that of the cell measured without the current collecting layer. This is due to the improved electrical connection between the cathode and external instrumentation provided by the presence of Pt layer which served as a good interfacial electronic conductor. All the spectra were fitted with the equivalent circuit (R1-CPE1)(R2-CPE2)(R3-CPE3)(R4-CPE4), where R and CPE respectively denoted as resistance and constant phase element. The impedance arcs obtained were allocated to the corresponding processes using the pseudo capacitance (C) value related to each arc that was referred to the literature (Baumann et al. 2006; Dailly et al. 2010; Ricote et al. 2012). As a result, R1 corresponds to the electrolyte response, while R2, R3 and R4 to the cathode processes. R1-CPE1 (higher frequency arc) corresponds to the contribution of the BCZY electrolyte which is considered for grain boundary response ($C \approx 10^{-10}$ F). R2-CPE2 ($C \approx 10^{-7}$ F) and R3-CPE3 ($C \approx 10^{-7}$ F), due to their capacitance value can be assigned to the charge transfer reaction which is the transfer of protons from the electrolyte to the electrode. The lower frequency arc, R4-CPE4 can be appointed to the oxygen dissociation/adsorption process due to the high capacitance value. The polarization resistance (R_p) of the cathodes is defined as the sum of R2, R3 and R4. The area specific resistance (ASR) of the cathodes is calculated using the relation $ASR = R_p \times S/2$, S being the cathode surface area and factor 1/2 was applied because the symmetrical cell is used. The ASR obtained for LSCF symmetrical cell measured at 700°C with and without Pt current collector is 0.87 and 31.25 Ωcm^2 , respectively. This preliminary electrochemical impedance study shows that the resistances obtained for the responses

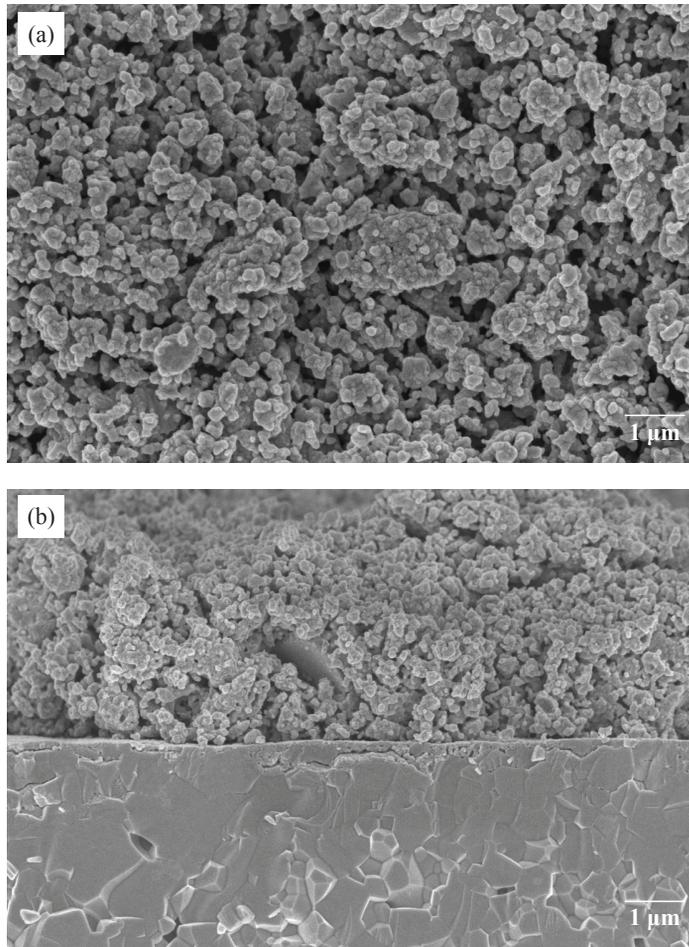


FIGURE 2. FESEM images of the a) surface and b) fractured cross-section of the LSCF|BCZY symmetrical cell

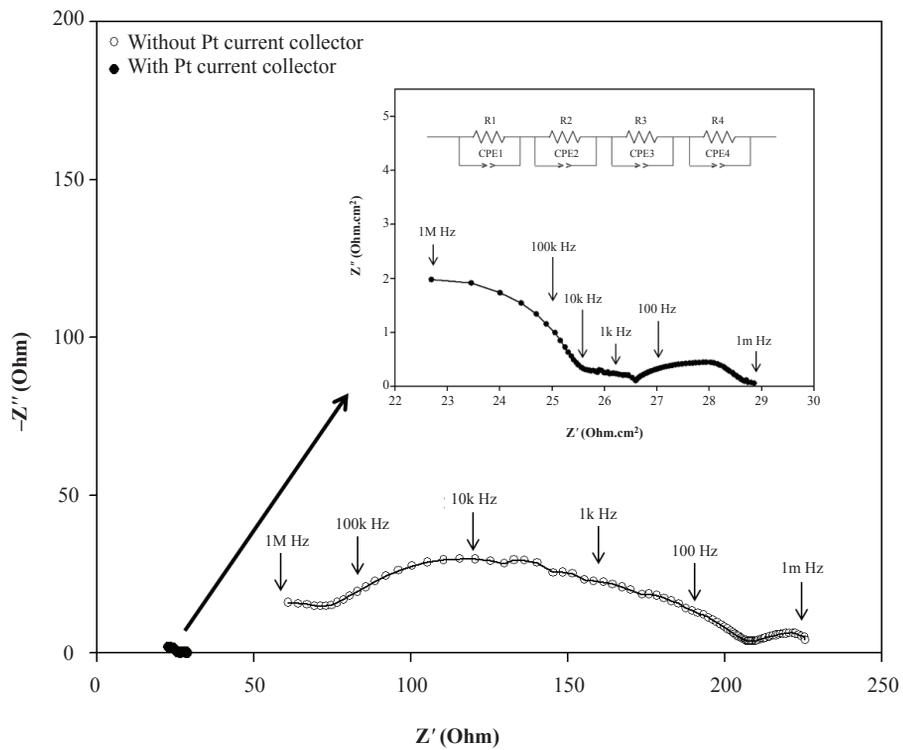


FIGURE 3. Impedance spectra of LSCF|BCZY|LSCF symmetrical cell measured at 700°C in air. Dots and solid lines are the experimental data and the fit using the equivalent circuit, respectively

are quite comparable with literature for the $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode coupled with $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte (Oda et al. 2014) signifying that the prepared LSCF is compatible with BCZY for potential application as a cathode material for PCFCs. Extensive works are still in progress to further increase the performance of LSCF|BCZY|LSCF cell by using others type of dispersion agents and composite cathode of LSCF-BCZY.

CONCLUSION

The LSCF powders had been successfully synthesized by an activated carbon assisted sol-gel method. Complete phase formation of LSCF was achieved at a calcination temperature of 700°C . The temperature obtained was considerably lower than the previous reported work of 900°C . The microstructural study showed a good contact between LSCF cathode and BCZY electrolyte at electrode/electrolyte interfacial layer which ensures a low contacting resistance. 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. The application of Pt current collecting layer on the symmetrical cell served as a good interfacial electronic conductor, which enhanced the electrochemical measurement process. An ASR of 0.87 and $31.25 \Omega\text{cm}^2$ is obtained, respectively, for the LSCF symmetrical cell measured with and without the presence of Pt current collector. The present results suggest the potential of LSCF as a promising cathode for PCFCs application.

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