



STRUCTURAL AND ELECTROCHEMICAL CHARACTERIZATIONS OF LANTHANUM-BASED COBALT FERRITE AND BARIUM CERATE-ZIRCONATE OXIDES AS COMPOSITE CATHODE FOR PROTON CERAMIC FUEL CELL APPLICATION

(Pencirian Struktur dan Elektrokimia Lantanum Berasaskan Kobalt Ferum Oksida dan Barium Serat-Zirkonat Oksida Sebagai Komposit Katod untuk Aplikasi Sel Fuel Seramik Proton)

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Abstract

The increased of cathode polarization resistance (R_p) in Proton Ceramic Fuel Cells (PCFCs) system is a major challenge in lowering their operating temperature. Therefore, selecting superior cathode materials is important to enhance the electrocatalytic activity of the electrode component. In this study, a composite cathode of $\text{LaSrCoFeO}_3\text{-BaCeZrYO}_3$ (LSCF-BCZY) with a ratio of 70:30 is chosen due to its advantages compared to pure LSCF. Dry pressing and spin coating techniques have been used to fabricate a 13-mm symmetrical half-cell with configuration of LSCF-BCZY|BCZY|LSCF-BCZY. The phase of sample is verified by an X-Ray Diffractometer (XRD). The electrochemical and microstructure of the half-cell is characterized using an Electrochemical Impedance Spectroscopy (EIS) and a Scanning Electron Microscope (SEM), respectively. At calcination temperature of 900 °C, the LSCF and BCZY components still preserved their single-phase structure as proven by XRD analysis. The half-cell demonstrated a thermally activated trend in a humidified atmosphere with area specific resistance (ASR) of 0.25 $\Omega\cdot\text{cm}^2$, 0.33 $\Omega\cdot\text{cm}^2$, 1.02 $\Omega\cdot\text{cm}^2$, 1.64 $\Omega\cdot\text{cm}^2$, and 5.75 $\Omega\cdot\text{cm}^2$ at temperature of 800 °C, 750 °C, 700 °C, 650 °C and 600 °C, respectively. An image of SEM reveals that the 10 μm LSCF-BCZY layer is well-adhered on the dense BCZY electrolyte surface. Therefore, the prepared LSCF-BCZY with the ratio of 70:30 demonstrated excellent characteristics as composite cathode for PCFCs application.

Keywords: composite cathode, single phase, spin coating, proton ceramic fuel cells

Abstrak

Peningkatan pada katod rintangan pengutuban (R_p) dalam sistem sel fuel seramik proton (PCFC) adalah cabaran terbesar untuk menurunkan suhu operasi. Oleh itu, pemilihan bahan katod yang terbaik adalah penting kepada meningkatkan aktiviti elektromangkin pada komponen elektrod tersebut. Dalam kajian ini, komposit katod daripada $\text{LaSrCoFeO}_3\text{-BaCeZrYO}_3$ (LSCF-BCZY) dengan nisbah 70:30 dipilih disebabkan kelebihannya berbanding dengan LSCF tulen. Teknik penekanan kering dan saduran berpusing telah digunakan untuk menghasilkan 13-mm sel separa simetri dengan konfigurasi iaitu LSCF-BCZY|BCZY|LSCF-BCZY. Pembentukan fasa sampel telah disahkan oleh pembelauan sinar-X (XRD). Sifat elektrokimia dan struktur mikro daripada sel separa simetri masing-masing telah dicari menggunakan spektroskopi impedans elektrokimia (EIS) dan pengimbasan mikroskop elektron (SEM). Pada suhu kalsin 900 °C, komponen LSCF dan BCZY tidak menunjukkan sebarang perubahan dan berfasa tunggal dibuktikan melalui analisis XRD. Sel ini menunjukkan kecenderungan aktif secara terma, yang disahkan melalui pengukuran EIS dalam atmosfera lembap dengan kawasan rintangan khusus (ASR) masing-masing iaitu 0.25 $\Omega\cdot\text{cm}^2$, 0.33 $\Omega\cdot\text{cm}^2$, 1.02 $\Omega\cdot\text{cm}^2$, 1.64 $\Omega\cdot\text{cm}^2$, dan 5.75 $\Omega\cdot\text{cm}^2$ pada suhu 800 °C, 750 °C, 700 °C, 650 °C dan 600 °C. Gambar SEM mendedahkan bahawa lapisan 10 μm LSCF-BCZY dipegang dengan baik pada permukaan elektrolit padat BCZY. Maka, penghasilan LSCF-BCZY dengan nisbah 70:30 menunjukkan ciri-ciri yang terbaik sebagai katod komposit bagi aplikasi PCFC.

Kata kunci: katod komposit, fasa tunggal, saduran berpusing, sistem sel fuel seramik proton

Introduction

A Proton Ceramic Fuel Cell (PCFC) has been categorized as a green energy device that converts reactant chemical energy to electrical energy with heat and water as a by-product for a high-power generation system. Nonetheless, a high cathode polarization resistance (R_p) significantly reduces overall cell system performance, particularly at intermediate temperature ranges [1]. The rising trend in R_p is related to the lack of a surface-active site for the oxygen reduction process (ORR) at the triple-phase boundary (TPB), which connects the electrolyte, cathode and gas phase. The selection of the best materials for the cathode component is crucial for the PCFC system because materials will exhibit different characteristics as they are couple with other materials and/or operates at elevated temperatures. Pure LaSrCoFeO_3 (LSCF) is a well-known cathode material for PCFCs because it contains excellent ionic and electronic charge carrier species than traditional cathodes [2]. However, due to the limitation of TPB sites formed in this pure LSCF then various methods and/or materials have been suggested to increase the TPB length [3,4] where one of them is by using a composite cathode [5].

Recently, the addition of some protonic species, for example Y^{3+} -doped $\text{Ba}(\text{Ce,Zr})\text{O}_3$ (BCZY) into the LSCF cathode is reported to lengthen the TPB using chemical

approaches with the best composition at 70:30 for LSCF to BCZY [6]. The symmetrical half-cell was built up for electrochemical studies to evaluate the behavior of materials. PCFC requires the optimum electrolyte substrate and cathode thin film design. The samples were dry pressed at the desired pressure and sintered at high temperatures to obtain the thick pellet. The study aims to characterize the structural of BCZY composite cathode powder after calcination and obtain electrochemical and microstructural data for composite LSCF coated on BCZY substrate. A button cell is used in EIS measurement to monitor material behavior and processing procedure for high system performance. A suitable equivalence circuit for EIS spectra is introduced to fit the electrochemical modelling procedure. The information from the fitting procedure is used to calculate capacitance, arc summit frequency, and ASR at intermediate temperatures. The Adler Lane Steel (ALS) model is used to explain the detailed mechanisms occur in each spectrum.

Materials and Methods

A modified sol-gel process was employed to produce LaSrCoFeO_3 cathode powder by dissolving all the metal nitrate salts in the universal solvent, followed by the addition of citric acid and ethylenediaminetetraacetic acid (EDTA). After alkalizing the solution with ammonium hydroxide solution to pH 9, ethylene glycol

was added to complete the reaction and the obtained brownish gel was calcined for 5 hours at 900 °C. The $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) single-phase powder and high relative density pellet (97.1%) were prepared as previously described [6]. To form the LSCF-BCZY composite cathode, the respective LSCF and BCZY powders was mixed at the ratio of 70:30 weight percent. The composite powder was transformed into cathode slurry and spin-coated both sites on BCZY pellet under optimized condition (2000 rpm for 30 seconds). The half-cell with configuration of LSCF-BCZY|BCZY|LSCF-BCZY was sintered at 600°C for 1 hours and 900°C for 3 hours.

An X-ray diffractometer (XRD), electrochemical impedance spectroscopy (EIS) and a scanning electron microscope (SEM) were used to characterize the prepared powder and half-cell, respectively. For XRD measurement, the LSCF-BCZY powder was radiated by Cu-K_α at ambient temperature with 1.5406 Å wavelengths using 8.04 keV energy (PANalytical X'Pert PRO MRD PW 3040). The scanning rate was set at 0.02 s^{-1} to collect the 2θ from 20° to 80°. The XRD data was analysed with X'Pert HighScore Plus software and compared to the Joint Committee on Powder Diffraction Standard (JCPDS) card number 089-1268 for LSCF and 01-089-2485 for BCZY. For electrochemical measurement, the symmetrical half-cell was subjected to the wet air with a flow rate of 90 mL/min. The measurement was made between 1 MHz and 10 mHz with amplitude voltage ranging from 3 to 5 mV at 600-800°C using the ZIVE SP2 Electrochemical Workstation (ZIVE LAB WonATech). An equivalence circuit of L_s - R_s (R_1Q_1)-(R_2Q_2) was applied for impedance spectrum analysis using ZIVE ZMAN™ 2.4 tool. The value of capacitance, arc summit frequency and polarization resistance for each temperature was calculated using the equation as reported by Malek et al. [7]. The raw and fitted data were both re-plotted using Origin 2019b. Scanning Electron Microscopy with Energy Dispersive X-ray (SEM/EDX) was used to evaluate the pellet's morphology after electrochemical testing. ImageJ software was used to measure the porosity of the SEM image.

Results and Discussion

Figure 1 depicts the XRD pattern of LSCF-BCZY composite cathode powder after calcined at 900 °C. All diffraction peaks were corresponded to JCPDS-card no. (LSCF ID: 01-089-1268) and (BCZY ID: 01-089-2485) with orthorhombic and cubic structures, respectively. The percentage formation of single perovskite phase was more than 90% for both LSCF and BCZY as calculated using Swarts and ShROUT equation indicates that the calcination temperature of 900 °C was sufficient to produce single-phase of samples. The prominent peaks were indexed using their Miller Indices (hkl) reflected plane as follows: (110), (020), (202), (220), (132), (224), and (332) for LSCF, and (110), (200), (211), (220), and (222) for BCZY. The lattice constants of LSCF and BCZY were also calculated using the Mathcad 14.0 software, and they are agreed with the reference data shown in Table 1. The obtained values were also close to that reported by Ismariza et. al. [8] for the LSCF-BCZY which calcined at $T=1000$ °C.

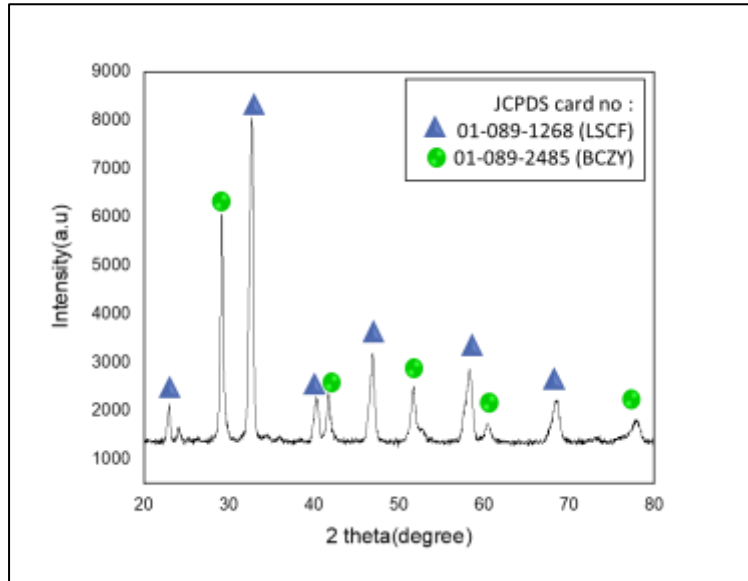


Figure 1. XRD pattern of the LSCF-BCZY composite cathode after calcined at $T = 900^{\circ}\text{C}$.

Table 1. Lattice parameter of the LSCF and BCZY taken from JCPDS-card and calculated ones using Mathcad 14 software

Sample ID	Lattice Parameter/Å (JCPDS-card)	Lattice Parameter/Å (Mathcad 14 software)
LSCF (Orthorombic)	$a = 5.475$	$a = 5.471$
	$b = 5.536$	$b = 5.482$
	$c = 7.848$	$c = 7.900$
BCZY (Cubic)	$a = 4.3436$	$a = 4.335$

Figure 2 shows the Nyquist impedance plot of the fabricated half-cell in humidified air at temperatures ranging from 600°C to 800°C . As the temperature increased, the size of the impedance spectrum became smaller which obeying the thermally activated behavior, as expected by Arrhenius's Law [9]. The arcs were resolved using an equivalent circuit as shown in the inset Figure 2. The first arc as represented by R_1Q_1 was referred to electronic charge transfer that occur at the cathode surface and the second arc, R_2Q_2 was associated to the ionic charge transfer reaction at the cathode/electrolyte interphase. The calculated capacitance which lies in the ranges of 4×10^{-2} - 10^{-4} for

R_1Q_1 circuit and 4×10^{-5} - 10^{-7} for R_2Q_2 circuit [10] signifies to the respective cathode process. Furthermore, the arc summit frequency confirmed the present of these two arcs at the middle and low frequency regions. The ASR values of $0.25 \Omega \cdot \text{cm}^2$, $0.33 \Omega \cdot \text{cm}^2$, $1.02 \Omega \cdot \text{cm}^2$, $1.64 \Omega \cdot \text{cm}^2$, and $5.75 \Omega \cdot \text{cm}^2$ were obtained at the temperature of 800°C to 600°C with the 50°C interval. The ASR values for pure LSCF increased by about one times higher than modified samples (800 - 600°C : $1.06 \Omega \cdot \text{cm}^2$, $1.13 \Omega \cdot \text{cm}^2$, $3.13 \Omega \cdot \text{cm}^2$, $6.50 \Omega \cdot \text{cm}^2$). The reduction of ASR values for LSCF-BCZY compared to pure LSCF indicates that the used of composite cathode has potential to enhance the performance of PCFC.

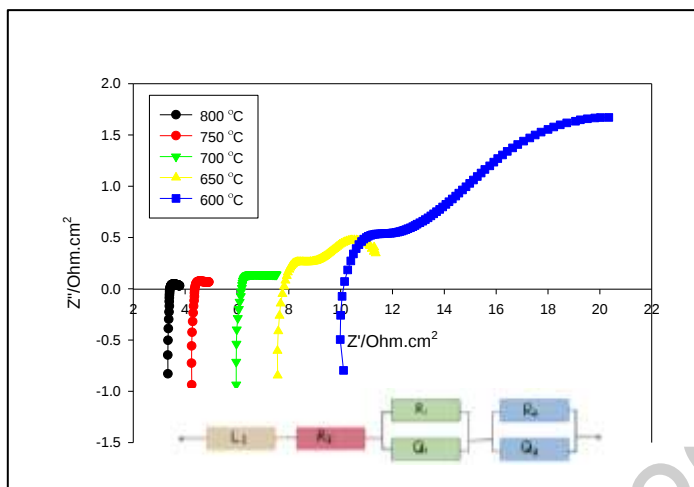


Figure 2. The EIS spectrum of LSCF-BCZY|BCZY|LSCF-BCZY under humidified air at the temperature in the range of 600 °C to 800 °C (Inset is the used equivalent circuit to resolve the associated responses)

Table 2. The calculated values of capacitance, arc summit frequencies and R_p and ASR for the LSCF-BCZY|BCZY|LSCF-BCZY

Temperature (°C)	Capacitance, C (Fcm ²)	Arc summit frequency, f° (Hz)	Polarization Resistance, R_p (Ω cm ²)	Area specific resistance, ASR (Ω cm ²)
800	C ₁ : 3.08x10 ⁻⁵ C ₂ : 2.58x10 ⁻²	f°_1 : 1.09x10 ⁴ f°_2 : 2.67x10 ³	R ₁ : 0.080 R ₂ : 0.420 R _p : 0.500	0.250
750	C ₁ : 2.39x10 ⁻⁵ C ₂ : 7.86x10 ⁻¹	f°_1 : 5.35x10 ⁶ f°_2 : 4.89x10 ³	R ₁ : 0.075 R ₂ : 0.589 R _p : 0.664	0.332
700	C ₁ : 1.02x10 ⁻⁵ C ₂ : 2.40x10 ⁻¹	f°_1 : 3.37x10 ⁵ f°_2 : 1.67x10 ²	R ₁ : 0.750 R ₂ : 1.290 R _p : 2.040	1.020
650	C ₁ : 3.11x10 ⁻⁶ C ₂ : 1.79x10 ⁻²	f°_1 : 2.81x10 ⁴ f°_2 : 3.16x10 ²	R ₁ : 0.800 R ₂ : 2.478 R _p : 3.278	1.639
600	C ₁ : 8.46x10 ⁻⁵ C ₂ : 1.79x10 ⁻²	f°_1 : 2.14x10 ⁴ f°_2 : 5.35x10 ²	R ₁ : 2.100 R ₂ : 9.400 R _p : 11.500	5.750

Figure 3 shows the SEM images of fractured cross-section and cathode surface of the LSCF-BCZY|BCZY|LSCF-BCZY symmetrical half-cell after

electrochemical measurement. There was no sign of crack and delamination occurring for the cell indicating a good adhesion between 10 μ m LSCF layer and dense

electrolyte which promotes a low contact resistance [11]. The cathode surface shows well dispersed and homogenized microstructure with porosity about 32%. This percentage is sufficient to allow better oxygen diffusion through the cathode material as the required porosity is in the range of 20% to 40% [12]. A good

adhesion between LSCF-BCZY cathode and BCZY electrolyte as well as the homogenized microstructure of the LSCF layer reduces the resistance of cathode bulk and leads to the fast surface oxygen ion diffusion [5, 13].

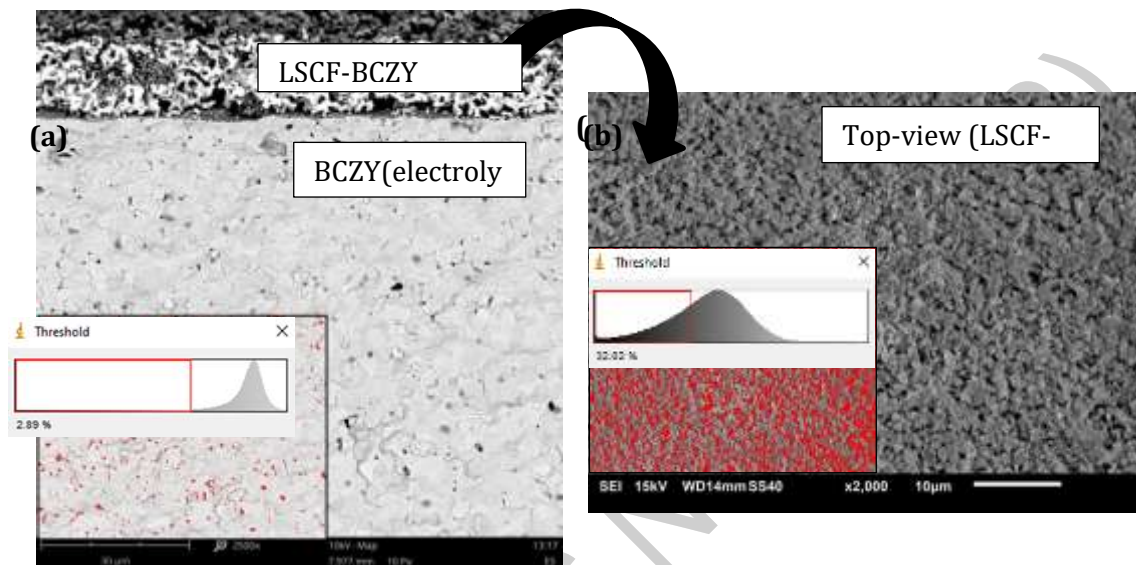


Figure 3. SEM images of the LSCF-BCZY|BCZY|LSCF-BCZY after electrochemical measurement (a) cross section and (b) top view of the cell

Conclusion

The LSCF and BCZY powders were successfully prepared by a sol-gel method using metals nitrate salts. Both compounds still maintained their respectively phase even after they were simultaneously calcined at 900 °C. The ASR value of 0.25 $\Omega \cdot \text{cm}^2$, 0.33 $\Omega \cdot \text{cm}^2$, 1.02 $\Omega \cdot \text{cm}^2$, 1.64 $\Omega \cdot \text{cm}^2$, and 5.75 $\Omega \cdot \text{cm}^2$ were reported at the intermediate temperature of 800°C to 600°C with the use of composite cathode half-cell. The well distributed and delamination-free cell morphology with optimized porosity is still preserved after electrochemical cell testing. The utilization of LSCF-BCZY composite cathode significantly reduce the polarization resistance of the fabricated cell signifying that it has a great potential and reliable for PCFC application.

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