

Electrochemical Performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Cathode Material Prepared by a Sol-gel Method Assisted with Functionalized Carbon Nanotubes

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ABSTRACT

A promising perovskite-type oxide ceramics of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode co-join with $\text{BaCe}_{0.56}\text{Zr}_{0.34}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCZY) as supported electrolyte for proton conducting fuel cell (PCFC) was investigated. The ultrafine LSCF was synthesized via a sol-gel process assisted with functionalized carbon nanotubes (f-CNTs) which served as a dispersing agent (denoted as modified-LSCF). The cathode ink of modified-LSCF was prepared by mixing cathode powder with binder that made up of ethyl cellulose and terpeniol. The cathode slurry was then deposited on both surface of the BCZY electrolyte via a spin coating technique to become a symmetrical half-cell. The half-cell of modified-LSCF|BCZY|modified-LSCF was subjected to Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX). The EIS data revealed the electrochemical reaction of the cell was a thermally activated process that follow the Arrhenius Law. LSCF incorporated with f-CNTs was effectively decreased the ASR value to $0.22 \Omega\text{cm}^2$ at 700°C , compared to $0.31 \Omega\text{cm}^2$ using pristine-LSCF. The pellet after EIS measurement showed no sign of crack and delamination at cathode/electrolyte interfaces, with optimum porosity obtained using ImageJ software and its elemental composition still preserved as observed by SEM/EDX analyses. Thus, the LSCF assisted with f-CNTs has a good potential to improve the quality of the cathode for high performance PCFC that operated at intermediate temperature.

Keywords: LSCF; symmetrical half-cell; electrical conductivity

INTRODUCTION

Proton conducting fuel cell (PCFC) is a promising clean energy system that converts chemical energy to electrical energy using fuel and oxidant gases. It can operate at intermediate temperature region (600°C - 800°C) compares to a high temperature ($> 800^\circ\text{C}$) conventional solid oxide fuel cell (SOFC). Reducing the operating temperature creates a massive problem especially at the cathode site and one of them is a high cathode polarization resistance [1, 2]. Tremendous efforts have been made to overcome the drawbacks and one of the approaches chosen is by tailoring the cathode microstructure using carbon based dispersing agent. A $\text{LaSrCoFeO}_{3-\delta}$ (LSCF) is a well-known mixed ionic electronic conductor (MIEC) cathode material that commonly used in PCFC. LSCF has a capability to create sufficient electrochemical reaction paths for electrolyte, electrode and gas phase. However, works on the tailoring of cathode microstructure are still needed to improve the PCFC performance. Addition of carbon-based compound (eg: activated carbon, graphite and carbon nanotubes) into LSCF mixtures in a sol-gel process is believed to alter the cathode microstructure which will facilitates the electrochemical reaction rates. However, the dispersion activity of carbon-

based material is low and surface modification is needed to prevent the agglomeration of cathode powder [3]. Thus, surface functionalization by means of acidification process via oxidation reaction has successfully changes the behavior of carbon-based from hydrophobic (water hating part) to the hydrophilic (water loving part) structure resulting to the homogenize dispersion and increasing the solubility of the material [4, 5]. From the best of our knowledge, LSCF modify with treated carbon based compound especially functionalized carbon nanotubes (f-CNTs) is rarely discussed and need to be explored. Herein in this work, f-CNTs were introduced as a dispersing agent into LSCF cathode prepared with a sol-gel method. The decrease in particle size to nano-range will increase the surface active site for vast electrochemical reaction. Consequently, by enlarging the surface active sites, the polarization resistance will greatly reduce.

MATERIALS AND METHODS

An amount of multiwalled carbon nanotubes (MWCNTs) was mixed with both monoprotic and diprotic acid in the ratio of 1:3 for oxidation process. To complete the process,

sonication, stirring and pH balanced were introduced. The wet samples was dried and known as functionalized carbon nanotubes (f-CNTs). The f-CNTs then served as a dispersing agent during synthesis of the LSCF cathode powder (denoted as modified-LSCF).

The high purity metal nitrate salts (La,Sr,Co,Fe) were respectively weighed and dissolved in 100 mL deionized water. Sufficient amount of citric acid and ethylenediaminetetraacetic acid (EDTA) were added into the aqueous media followed by 4 mg of f-CNTs to attain the disperse activity of the compound. The mixtures was then adjusted to pH 9 using ammonium hydroxide solution to promote an alkaline media and followed by addition of ethylene glycol. The sol was pre-heated until became a gel and dried at 150°C for 15 hours. The black solid was calcined at 900°C for 5 hours to produce a modified $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) powder. The same procedures have been repeated to prepare LSCF without addition of f-CNTs and labelled as pristine-LSCF.

Prior to the measurement of cathode performance, the $\text{BaCe}_{0.36}\text{Zr}_{0.54}\text{Y}_{0.1}\text{O}_{3-\delta}$ electrolyte powder was prepared via combined citrate-EDTA complexion sol-gel method as reported by Abdullah et al [6]. Then a symmetrical half-cell of pristine-LSCF|BCZY|pristine-LSCF and modified-LSCF|BCZY|modified-LSCF were fabricated using dry pressing (for BCZY) and spin coating (for pristine-LSCF and modified-LSCF) techniques before sintered at 950°C. Each of the cell was characterized using Electrochemical Impedance Spectroscopy (EIS) in wet air by bubbling the synthetic air via deionized water at room temperature. The EIS spectra were recorded in the frequency range from 1 MHz to 10 mHz with an increment of temperature from 650°C to 800°C. For impedance analysis, equivalence circuit of $\text{Rs}(\text{R}_1\text{Q}_1)(\text{R}_2\text{Q}_2)(\text{R}_3\text{WQ}_3)$ was selected and the detailed mechanisms occur in the symmetrical half-cell was explained using ALS model. Morphology and elemental analysis of the pellet was observed using Scanning Electron Microscopy with Energy Dispersive X-ray (SEM/EDX). From the SEM micrograph, the porosity was evaluated using ImageJ software.

RESULTS AND DISCUSSION

EVOLUTION OF SPECTRUM

Figure 1 shows the EIS spectra for the both of modified-LSCF and pristine-LSCF that performed under humidified air at the temperature of 650°C to 800°C. The spectra can be generally divided into 3 regions which are high frequency regime 1MHz – 1kHz, middle frequency regime 1kHz – 1Hz and low frequency regime 1Hz – 10mHz. At temperature above than 600°C, the present of inductive tail due to the connecting wires used as a connector was clearly appeared at high frequency region. At high temperature, this response can be omitted during impedance analysis because the impedance arcs were governed by electrode responses [7, 8] and the arcs also mainly dominated by the electrode responses since no longer electrolyte responses appeared.

Clearly seen the size of the spectrum decreased as the temperature increased indicating that the electrochemical reaction process at cathode site is a thermally activated process and such inverse proportion obeys the Arrhenius Law [9].

IMPEDANCE ANALYSIS

The impedance analysis expressed the mechanism of the individual physical and chemical processes occur in the spectrum and also one of the techniques used to interpret the complex electrochemical reaction. In order to distinguish the corresponding process in the overlapping arc, the Adler Lane Steele (ALS) model was referred where the cathode contribution consists of three arcs that correspond to cathode interface, cathode and, electrolyte grain boundary and cathode bulk [10]. Figure 2 demonstrates the fitted EIS spectrum of the (a) modified-LSCF and (b) pristine-LSCF measured at 700°C under humidified air condition. The spectrum's responses were separated using an equivalent circuit of $\text{Rs}(\text{R}_1\text{Q}_1)(\text{R}_2\text{Q}_2)(\text{R}_3\text{WQ}_3)$ as shown in Figure 2(c), where R_s is the total ohmic loss that refers to electrolyte resistance, R_1Q_1 and R_2Q_2 indicate the cathode reaction processes. The existence of Warburg element in third arc due to the 45° angle present to this particular spectrum based on ALS model and turned to R_3WQ_3 .

Table 1 represented the values of R, Q and W which correspond to resistance, constant phase element (CPE) and Warburg element. Values of capacitance, arc summit frequencies, polarization resistance (R_p) and area specific resistance (ASR) for each spectra were calculated using equation 1 to equation 4. The obtained results was comparable with the work by Ali et al and Haanappel et al [11, 12]. Each capacitance value obtained signifies to the respective cathode process. The value obtained at the first arc denoted as R_1Q_1 refer to electronic charge transfer that occur at the cathode surface and R_2Q_2 indicate the ionic charge transfer reaction at the cathode/electrolyte interface. Dailly et al has set the acceptable range for that particular region was approximately from 4×10^{-3} to 10^{-7} Fcm^2 [13]. The arc summit frequency confirmed the present of these two arcs at the middle frequency region. At low frequency region, the R_3WQ_3 was assigned to oxygen dissociation or adsorption process on the cathode surface and diffusion of oxygen ion at cathode bulk that gives the capacitance value in the range of 3×10^{-3} to 10^{-1} Fcm^2 [13].

It was also observed that increasing the frequency lead to the reduction of the resistance values and the electrolyte arc became small. Therefore, the adsorption, dissociation and diffusion process of oxygen species was restricted to cathode reaction at 700°C. The same analyses of cathode materials based on this model were also reported by Adler et al, Kim et al and also Baek et al [14-16]. The obtained ASR value decreased from $0.31 \text{ } \Omega\text{cm}^2$ (pristine-LSCF) to $0.22 \text{ } \Omega\text{cm}^2$ (modified-LSCF). Thus, the modified-LSCF with the help of f-CNTs has been successfully lowering the ASR value and increased the cathode performance.

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

$$f^o = \frac{1}{2\pi RC}$$

$$Rp = Rc \times A(\pi r^2)$$

$$ASR = \frac{Rp}{2}$$

- (1) Figure 3 shows the SEM images of cross section and surface of the both of pristine-LSCF (a,b) and modified-LSCF (c,d) after the EIS measurement. Both of the cathode surfaces showed a well distributed particles with the porosity of $32.5\% \pm 0.3\%$ for pristine-LSCF and $34.2\% \pm 0.2\%$ for modified-LSCF using the ImageJ software. These values are in the acceptable range since the optimum porosity reported in literature was in the range of 20% to 40%, which is ideal for oxygen diffusion rate through the cathode material. A good adhesion between LSCF cathode and BCZY electrolyte was also observed as no sign of crack
- (2)
- (3)
- (4)

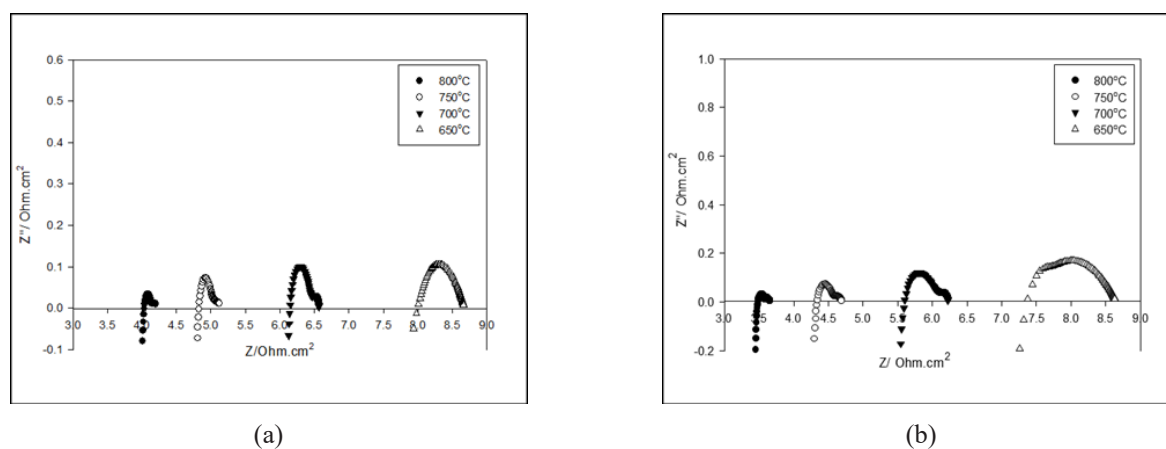


FIGURE 1. Evolution of the EIS spectra of (a) modified-LSCF and (b) pristine-LSCF in atmosphere containing humidified air

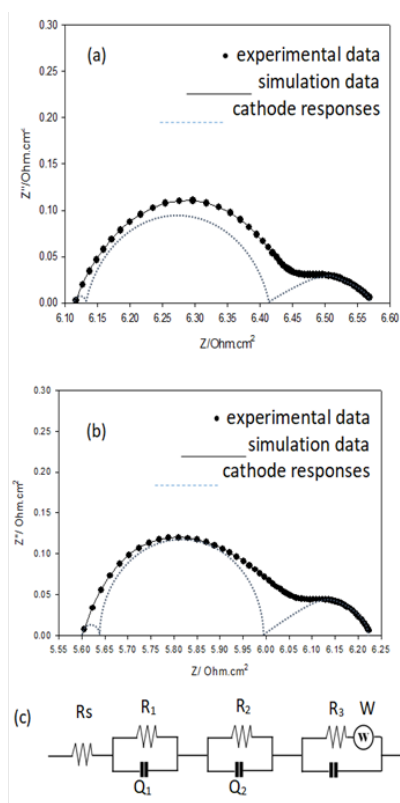


FIGURE 2. The EIS spectrum of (a) modified-LSCF and (b) pristine-LSCF measured in humidified air at 700°C and (c) equivalent circuit used to fit the experimental data

TABLE 1. The calculated values of capacitance, arc summit frequencies and R_p for both pristine-LSCF and modified-LSCF at 700°C

Cathode	Capacitance, C (Fcm ²)	Arc summit frequency, f° (Hz)	Resistance, R (Ω cm ²)	Area specific resistance, ASR (Ω cm ²)
pristine-LSCF	$C_1 = 1.02 \times 10^{-6}$	$f_1^{\circ} = 3.16 \times 10^4$	R1= 0.05	0.31
	$C_2 = 9.52 \times 10^{-5}$	$f_2^{\circ} = 3.162 \times 10^3$	R2= 0.27	
	$C_3 = 3.68 \times 10^{-2}$	$f_3^{\circ} = 1.26 \times 10^1$	R3= 0.30	
			$R_p = 0.62$	
modified-LSCF	$C_1 = 3.13 \times 10^{-6}$	$f_1^{\circ} = 2.01 \times 10^4$	R1= 0.04	0.22
	$C_2 = 8.46 \times 10^{-5}$	$f_2^{\circ} = 4.89 \times 10^3$	R2= 0.17	
	$C_3 = 1.79 \times 10^{-2}$	$f_3^{\circ} = 2.67 \times 10^1$	R3= 0.23	
			$R_p = 0.44$	

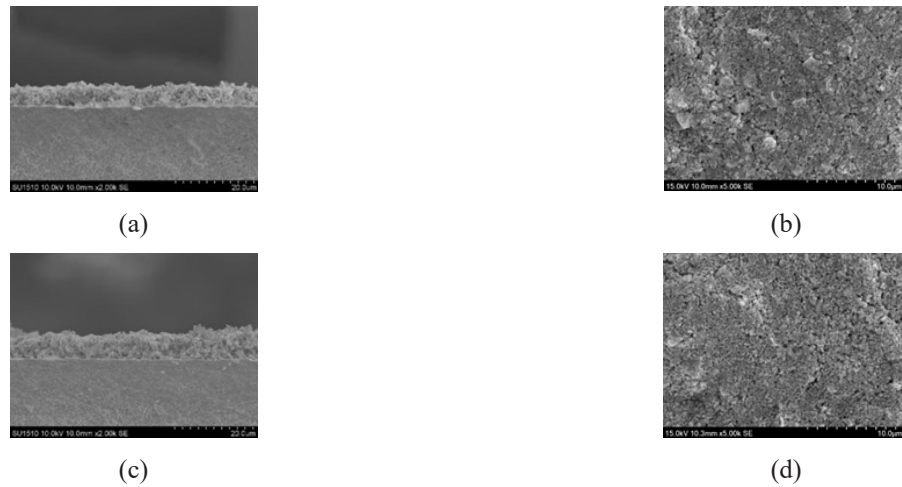


FIGURE 3. SEM images of the cross-section and cathode surface of the symmetrical half-cell of (a,b)pristine-LSCF and (c,d) modified-LSCF after EIS analysis.

TABLE 2. The elemental composition of (a) pristine-LSCF | BCZY | pristine-LSCF and (b) modified-LSCF | BCZY | modified-LSCF

Symmetrical cell	Element	Nominal ratio	Experimental ratio	
(a)pristine-LSCF BCZY pristine-LSCF	La	0.60	0.58	
	Sr	0.40	0.37	
	Co	0.20	0.15	
	Fe	0.80	0.75	
	O	2.7	1.78	
	Ba	1.00	0.97	
	Ce	0.54	0.51	
	Zr	0.36	0.32	
	Y	0.10	0.08	
	(b) modified-LSCF BCZY modified-LSCF	O	2.7	2.01
		La	0.60	0.59
Sr		0.40	0.38	
Co		0.20	0.16	
Fe		0.80	0.77	
O		2.7	2.31	
Ba		1.00	0.98	
Ce		0.54	0.52	
Zr		0.36	0.35	
Y		0.10	0.09	
O	2.7	2.28		

and delamination [17,18] occurred at cathode/electrolyte interface.

The elemental analysis for the symmetrical half-cell was performed using EDX analysis as tabulated in Table 2. The elemental composition for cathode layer after the EIS analysis was comparable with the nominal ratio of LSCF; La=0.6, Sr=0.4, Co=0.2 and Fe=0.8. Nevertheless, the experimental ratio for BCZY element was also almost identical with the nominal one that are Ba=1.00, Ce=0.54, Zr=0.36 and Y=0.10. Thus, this elemental composition clarify that the thermal treatment applied during the operating temperature do not alter the elemental composition in the compound.

CONCLUSION

ALS model has successfully described the cathode reaction mechanism occur in the symmetrical half-cell of pristine-LSCF | BCZY | pristine-LSCF and modified-LSCF | BCZY | modified-LSCF. Addition of f-CNTs to the LSCF material has effectively decreased the ASR value from $0.31 \Omega\text{cm}^2$ (pristine-LSCF) to $0.22 \Omega\text{cm}^2$ (modified-LSCF). The good morphology, optimum porosity as well as elemental composition were still preserved after the EIS measurement. Thus, modification of LSCF cathode using f-CNTs shows a good candidate to increase the electrochemical performance for proton conducting fuel cell.

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DECLARATION OF COMPETING INTEREST

None.

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