Electrochemical performance of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ cathode in air and wet air for BaCe$_{0.54}$Zr$_{0.36}$Y$_{0.1}$O$_3$-based proton-conducting solid oxide fuel cell

Abdullah Abdul Samat$^{1,2}$, Mahendra Rao Somalu$^{1,*}$, Andanastuti Muchtar$^{1,3}$ and Nafisah Osman$^{4}$

$^1$ Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
$^2$ Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Kampus UniCITI Alam, Sungai Chuchuh, Padang Besar 02100, Perlis, Malaysia
$^3$ Centre for Materials Engineering and Smart Manufacturing, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
$^4$ Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia

*Corresponding author e-mail: mahen@ukm.edu.my

Abstract. Solid oxide fuel cells (SOFC) with proton-conducting electrolytes (H$^+$–SOFC) exhibit better performance than SOFC with oxygen ion-conducting electrolytes (O$_2$–SOFC) at intermediate-temperatures (500 – 800 °C). Thus, humidity-resistant cathode materials, particularly for H$^+$–SOFC application must be developed. An ideal cathode for intermediate temperature H$^+$–SOFC should simultaneously conduct...
proton (H\(^+\)), oxygen ion (O\(^2-\)) and electron (e\(^-\)) to enlarge the triple-phase boundary (TPB) to the whole cathode and improve the intermediate-temperature H\(^+\)–SOFC performance [1].

A number of perovskite-type oxide mixed ionic-electronic conducting materials (MIEC) with ABO\(_3\) structure have been developed as H\(^+\)–SOFC cathode materials [2–5]. One of the MIEC materials is lanthanum strontium cobaltite (La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\)) (LSC). Wang et al. [6] used LSC as cathode materials for H\(^+\)–SOFC based on yttrium-doped barium cerate-zirconate (BaC\(_x\)Zr\(_x\)Y\(_{1-x}\)) (BCZY). However, this study focused on modifying the LSC structure from MIEC to composite cathodes as to improve LSC electrochemical performance. Limited studies have been reported on the electrochemical performance or conducting properties of LSC in different atmospheres, particularly for its application as cathode in H\(^+\)–SOFC. Different atmospheric conditions result in different electrochemical properties of a cathode material. Therefore, the aim of this work is to evaluate the electrochemical and conducting properties of LSC material in air and wet air at intermediate-temperatures for cathode application in H\(^+\)–SOFC based on BaCe\(_{0.55}\)Zr\(_{0.35}\)Y\(_{0.1}\)O\(_3\) (BCZY) proton-conducting electrolyte.

2. Materials and methods

2.1. Powder preparation and characterisation

Cathode powder of La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\) (LSC) was prepared by citrate-ethylenediaminetetraacetic acid (EDTA) sol-gel method using ethylene glycol (EG) as polymerising agent. A stoichiometric mixture of the starting materials was dissolved in deionised water to produce a solution of metal nitrate salts. Stoichiometric amounts of citric acid and EDTA were added into the solution and was followed by adjusting the pH value of the mixture to 0.5. The mixture was then added with EG and slowly heated at 100 – 150 °C to evaporate the water and obtain a viscous gel. The obtained gel was dried at 150 °C up to 250 °C. The produced black as-synthesised powder was ground and calcined at 900 °C for 5 h. The details for the preparation of LSC powder were reported elsewhere [7].

To confirm the formation of LSC perovskite phase, the calcined powder was subjected to X-ray diffractometry (XRD) analysis by using Bruker D8-Advance XRD machine within the 2θ range of 20° to 80°. BET surface area and porosity analyser of Micromeritics ASAP 2020 was used to determine the BET surface area (S\(_{\text{BET}}\)) of the calcined powder. A Zeiss Merlin Compact field-emission scanning electron microscope (FESEM) was used to examine the morphology of the calcined powder. ImageJ software was used to determine mean particle size (D\(_{\text{SEM}}\)) by statistical analysis of 100 particles in the FESEM image.

2.2. Symmetrical cell fabrication and characterisation

Single-phase BCZY electrolyte powder was also synthesised by citrate-EDTA sol-gel method [8]. The synthesised BCZY powder was prepared into a 13 mm-diameter pellet by pressing the calcined BCZY powder at 1100 °C using a uniaxial hydraulic pressing machine. The BCZY green pellet was sintered at 1400 °C for 10 h to obtain a high-density BCZY pellet. The calcined LSC cathode powder was ballmilled with Hypermer KD15 (dispersant) in acetone for 5 h and dried in a drying oven at 90 °C overnight. To produce LSC cathode slurry, the LSC dried powder was mixed with terpineol and ethyl cellulose. The mixture was ground in an agate mortar for 10 min and followed by milling the ground mixture using a triple-roll mill for 30 min. The details for the preparation of the LSC cathode slurry were reported elsewhere [9]. A symmetrical cell of LSC|BCZY|LSC was fabricated by screen-printing the prepared LSC cathode slurry onto both surfaces of the sintered BCZY electrolyte pellet. The fabricated LSC|BCZY|LSC symmetrical cell was sintered at 900 °C for 2 h.

ZIVE SP2 electrochemical workstation (ZIVELAB WonATech, Korea) was used to measure the electrochemical characteristics of the sintered symmetrical cell. The measurement was performed at 500 °C to 800 °C in air and wet air within the frequency range of 0.1 Hz to 1 MHz under open-circuit conditions with a sinusoidal voltage of 5 mV. ZMAN™ 2.2 f3 software (ZIVE LAB) was used to analyse the electrochemical impedance testing data and the impedance diagram was plotted in real impedance (Z\(_{\text{real}}\) or Z\(_r\)) versus imaginary impedance (Z\(_{\text{imag}}\) or Z\(_i\)). Area specific resistance (ASR) was calculated using the following equation: ASR = (R\(_p\)×A)/Z, where R\(_p\) refers to the resistance or polarisation resistance at the cathode|electrolyte interfacial layer, and A refers to the specific cathode.
active area (0.50 cm²). A Hitachi U1510 scanning electron microscope (SEM) was used to capture the microstructure image of the symmetrical cell at the cross-section and the cathode film surface after electrochemical characteristics measurement.

3. Results and discussion

3.1. Properties of the prepared powder and symmetrical cell

The XRD spectrum of the as-synthesised powder after calcination at 900 °C for 2 h is shown in Figure 1(a). The calcined powder exhibited a single-phase of LSC perovskite as confirmed by the XRD measurement. All the prominent peaks in the XRD spectrum of the calcined powder were matched with the ICDD reference code 00-048-0121 (structure: cubic; space group: Pm-3m). The peaks were accordingly indexed to their Miller indices (hkl) of (100), (110), (111), (200), (210), (220), (300) and (310). The typical particle morphology image of the calcined powder is shown in the SEM micrograph in Figure 1(b). The calcined powder consists of homogeneously shaped particles that are connected to one another. The calculated values of lattice parameter (a), crystallite size (D_{110}), density (ρ), BET surface area (S_{BET}) and mean particle size (D_{SEM}) of the calcined powder are tabulated in Table 1. Figure 2 shows the SEM micrographs at surface and cross-section of LSC|BCZY|LSC symmetrical cell. The screen-printed cathode layer with thickness of 3.90 ± 0.18 μm was well adhered and homogeneously distributed onto the electrolyte substrate, as shown in the SEM micrographs. A sufficient porous structure of the cathode (porosity = 23.09 ± 0.42 %) was also observed in the SEM micrographs.

![Figure 1](image1.png)

**Figure 1.** Images of (a) XRD spectrum and (b) SEM micrograph of the calcined powder at 900 °C

| Value                  | a (Å) | D_{110} (nm) | ρ (g cm⁻³) | S_{BET} (m² g⁻¹) | D_{SEM} (μm) |
|------------------------|-------|--------------|------------|-----------------|--------------|
| a (Å)                  | 3.84  | 18.71        | 6.30       | 8.68            | 0.26 ± 0.06  |

3.2. Electrochemical property analysis

Electrochemical impedance spectrum of the fabricated LSC|BCZY|LSC symmetrical cell measured at different temperatures in air and wet air is shown in Figure 3. The impedance arcs became small, indicating that the total resistance of the sample decreased with increasing temperature from 500 °C to 800 °C. This observation is in line with the electrolyte ohmic resistance (R_{ohm}) and cathode ASR values of the symmetrical cell measured in air and wet air at different temperatures (Table 2).
Figure 2. SEM images at cross-section and surface of LSC|BCZY|LSC symmetrical cell

Figure 3. Impedance spectrum of LSC|BCZY|LSC symmetrical cell measured in (a) air and (b) wet air at different temperatures; and (c) normalised impedance spectrum of the symmetrical cell measured in air and wet air at 700 °C
The formation of OH\(_{\text{•}}\) due to water molecule reaction between (O\(_{\text{•}}\)) vacancies and produces proton (H\(_{\text{•}}\)) as shown in equation (1). The second step is a hydration process producing hydroxyl ion (OH\(_{\text{•}}\)), which can modify the concentration of holes or oxygen vacancies, thereby changing the resultant electrical properties of a cathode material. The presence of OH\(_{\text{•}}\) also helps enlarge the active sites for water molecule formation in the bulk cathode and at the cathode/electrolyte interface or TPB [2,11]. Conversely, the limited active sites for water molecule formation at TPB only provide a high ASR value of the MIEC cathode in air [11,12].

The formation of OH\(_{\text{•}}\) may comprise two steps. The first step is the reaction between oxygen vacancies (V\(_{\text{O}}\)) and adsorbed water molecule (H\(_2\)O(ad)). The reaction fills the lattice positions of oxide ion (O\(_{\text{•}}\)) vacancies and produces proton (H\(_{\text{•}}\)) interstitial as shown in equation (1). The second step is a reaction between (O\(_{\text{•}}\)) and (H\(_{\text{•}}\)) interstitial, producing OH\(_{\text{•}}\) as shown in equation (2). Formation of water molecules is shown in equation (3) [2,13].

\[
\begin{align*}
H_{\text{ad}}(O) + V_{\text{O}}^\text{ad} & \leftrightarrow O_{\text{ad}}^\text{ad} + 2H^+ \quad (1) \\
H^+ + O_{\text{ad}}^\text{ad} & \leftrightarrow OH_{\text{ad}}^\text{ad} \quad (2) \\
O_{2(g)} + 4OH_{\text{ad}}^\text{ad} + 4e^- & \rightarrow 2H_2O_{(g)} + 4O_{\text{ad}} \quad (3)
\end{align*}
\]

At 500 °C, the resistance or ASR value is higher in wet air than in air. The high ASR value is due to excessive H\(_2\)O(ad) on the LSC cathode surface. The excessive H\(_2\)O(ad) leads to competitive adsorption between H\(_2\)O(ad) and O\(_2\) on the cathode surface. The competitive adsorption reduces the O\(_2\) transport/absorption process into the cathode and TPB, leading to a slower ORR process and increased cathode polarisation resistance [5,14]. Excessive H\(_2\)O(ad) and competitive adsorption commonly occur at a low temperatures ranging from 450 °C to 650 °C [2-4]. The activation energy (E\(_a\)) value of LSC (0.70 eV) is similar to that of Pr\(_{0.58}\)Sr\(_{0.42}\)Fe\(_{0.8}\)Co\(_{0.2}\)O\(_{3-\text{δ}}\) [5] and lower than that of LSC-BaZr\(_{0.1}\)Ce\(_{0.7}\)Y\(_{0.2}\)O\(_{3-\text{δ}}\) (E\(_a\) = 1.32 eV) [6], SrFe\(_{1.3}\)Mo\(_{0.7}\)O\(_{3-\text{δ}}\)-BaZr\(_{0.1}\)Ce\(_{0.7}\)Y\(_{0.2}\)O\(_{3-\text{δ}}\) (E\(_a\) = 1.28 eV) [15] and BaCe\(_{0.4}\)Sm\(_{0.6}\)Fe\(_{0.8}\)O\(_{3-\text{δ}}\) (E\(_a\) = 1.43 eV) [1]. All of the aforementioned materials are developed as cathodes for H\(^+\)/O\(^2-\)/e\(^-\) application, and all the E\(_a\) values are recorded in wet air. The lower ASR value in wet air than in air and the low E\(_a\) value in wet air suggest that LSC is a hybrid MIEC O\(^3-\)/e\(^-\) and MIEC H\(^+\)/O\(^2-\)/e\(^-\) material. LSC can then be proposed as one of the triple conducting H\(^+\)/O\(^2-\)/e\(^-\) materials for

| Temperature (°C) | ASR (Ω cm\(^{-2}\)) | R\(_\text{slim}\) (Ω) |
|-----------------|---------------------|-----------------|
|                 | In air   | In wet air | In air   | In wet air |
| 500             | 0.98     | 1.50      | 130.92   | 111.01    |
| 600             | 0.70     | 0.35      | 56.60    | 48.3      |
| 700             | 0.48     | 0.30      | 26.90    | 25.36     |
| 800             | 0.11     | 0.06      | 14.01    | 13.85     |

Table 2. Area specific resistance (ASR) and ohmic resistance (R\(_\text{slim}\)) values of the LSC|BCZY|LSC symmetrical cell measured in air and wet air at different temperatures.
cathode application in H⁺–SOFC. However, further investigation of the hybrid conducting properties of LSC must be conducted.

4. Conclusions
Electrochemical performance of sol-gel derived LSC cathode material was evaluated using screen-printed symmetrical cell of LSC|BCZY|LSC in air and wet air at intermediate temperatures (500 °C – 800 °C). The $R_p$ or ASR of the cathode and $R_{ohm}$ of the electrolyte decreased as the temperature increased from 500 °C to 800 °C in air and wet air environments. The values of ASR are lower in wet air than in air at 600 °C, 700 °C and 800 °C, and the values of $R_{ohm}$ are lower in wet air than in air at 500 °C, 600 °C, 700 °C and 800 °C. The lower values of $R_{ohm}$ and ASR in wet air at the aforementioned temperatures could be attributed to the hydration and the increase in proton conduction in the BCZY proton-conducting electrolyte and LSC cathode. However, at a low temperature (500 °C), the ASR value is higher in wet air than in air due to the excess water molecules covering the surfaces of the LSC cathode. Overall, the fabricated LSC cathode material exhibit better electrocatalytic activity in wet air than in air at 600 °C to 800 °C. The low ASR value and $E_v$ value in wet air suggests that LSC is a preferential cathode material for H⁺–SOFC with BCZY electrolyte.

Acknowledgements
This work has been supported by the Universiti Kebangsaan Malaysia (UKM) via Research University Grant (GUP-2016-005). The authors would like to extend their gratitude to the Centre for Research and Instrumentation Management (CRIM) of UKM, Universiti Teknologi MARA (UiTM) and Universiti Tun Hussein Onn Malaysia (UTHM) for the excellent facility support. Abdullah Abdul Samat is grateful to Ministry of Higher Education (MOHE) of Malaysia and Universiti Malaysia Perlis (UniMAP) for the SLAB/SLAI PhD scholarship.

References
[1] Zhang C, Du Z, Zhao H and Zhang X 2013 Electrochimica Acta 108 369
[2] Zhu A, Zhang G, Wan T, Shi T, Wang H, Wu M, Wang C, Huang S, Guo Y, Yu H and Shao Z 2018 Electrochimica Acta 259 559
[3] Sun S and Cheng Z 2017 J. Electrochem. Soc. 164 F81
[4] Yang Z, Liu Y, Chen Y, Wang J, Han Z, Zhu Y and Han M 2017 Int. J. Hydrog. Energy 42 6997
[5] Vert VB, Solis C and Serra JM 2010 Fuel Cells 11 81
[6] Wang MS, Wang JX, He CR, Xue YJ, Miao H, Wang Q and Wang WG 2015 Ceram. Int. 41 5017
[7] Abdul Samat A, Somalu MR, Muchtar A, Hassan OH and Osman N 2016 J. Sol-Gel Sci. Technol. 78 382
[8] Abdullah NA, Hasan S and Osman N 2013 J. Chem. 2013 1
[9] Abdul Samat A, Jais AA, Somalu MR, Osman N, Muchtar A and Lim KL 2018 J. Sol-Gel Sci. Technol. 86 617
[10] Fan L, Zhang H, Chen M, Wang C, Wang H, Singh M and Zhu B 2013 Int. J Hydrog. Energy. 38 11398
[11] Dailly J, Fourcade S, Largeteau A, Mauvy F, Grenier JC and Marrony M 2010 Electrochimica Acta 55 5847
[12] Fan L and Su P-C 2016 J. Power Sources 306 369
[13] Batocchi P, Mauvy F, Fourcade S and Parco M 2014 Electrochimica Acta 145 1
[14] Lee K-C, Choi M-B, Lim D-K, Singh B and Song S-J 2013 J. Power Sources 232 224
[15] Li M, Ni M, Su F and Xia C 2014 J. Power Sources 260 197