Phase formation and microstructure analyses of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$-$\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ composite material prepared by solid state mixing method

Abdullah Abdul Samat$^{1,2,3,*}$, Muhammad Syafiq Amsyar Ahmad Pisor$^{1}$, Meor Ahmad Faris Meor Ahmad Tajudin$^1$, Mohd Al-Hafiz Mohd Nawi$^1$, Murizam Darus$^2$, Nafisah Osman$^4$ and Nurul Akidah Baharuddin$^5$

$^1$Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Kampus UniCITI Alam, Sungai Chuchuh, Padang Besar 02100, Perlis, Malaysia.
$^2$Centre of Excellence for Unmanned Aerial Systems (CEOUAS), Universiti Malaysia Perlis (UniMAP), 01000 Kangar, Perlis, Malaysia.
$^3$School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), 02600 Arau, Perlis, Malaysia.
$^4$Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia.
$^5$Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

Abstract. A composite material of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$-$\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (LSC-BCZY) was prepared by mixing sol-gel derived LSC and BCZY powders in different weight percentage (wt%) ratio of LSC to BCZY (LSC:BCZY). The prepared composite powders were denoted as S1 (30:70), S2 (50:50) and S3 (70:30). The powders were characterized by an X-ray diffractometer (XRD), a Brunauer-Emmett-Teller (BET) surface area and porosity analyzer and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. XRD analysis confirmed that all of the powders were not pure enough due to the presence of impurity phases such as barium carbonate (BaCO$_3$) and strontium carbonate (SrCO$_3$) and unknown phases. S1 powder has the highest amount of impurity phases (81.19%) and the largest BET surface area (4.82 m$^2$ g$^{-1}$). All of the powders formed typical clump-like network structure as proven by SEM analysis. EDX analysis revealed that the elemental compositions of La, Sr and Zr were deviated from their nominal mole fractions in all powders due to the Zr-rich clusters formation. The results indicate that the formation of pure and homogenous LSC-BCZY composite powder prepared by solid state mixing method requires further modification and improvement of the preparation method.

1 Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device that converts chemical energy directly into electricity via electrochemical processes, producing water molecule and high quality of heat as by-products. Generally, an SOFC consists of three major components

* Corresponding author: abdullahabdul@unimap.edu.my
which are electrolyte, electrodes (anode and cathode) and interconnect. Nowadays, SOFC with proton-conducting electrolyte (H\(^+\)-SOFC) has received greater attention than SOFC with oxide ion-conducting electrolyte (O\(^2-\)-SOFC) due to its advantages including higher ionic conductivity and electrical efficiency at SOFC operating temperature range (500 °C - 800 °C) [1,2]. Performance of an SOFC either H\(^+\)-SOFC or O\(^2-\)-SOFC is strictly determined by the properties of its components such as purity, porosity, homogeneity and conductivity [3–5].

One of the most crucial components of an SOFC is the cathode as the low performance of an SOFC is closely related to the cathode polarization resistance (R\(_p\)) and degradation [6–8]. To minimize the cathode R\(_p\) issue, cathode materials for an SOFC must have high electrical conductivity (> 100 S cm\(^{-1}\)) and adequate porosity (20 - 40 %), stable in working environment as well as chemically and thermally compatible with other components. In addition, the most important criterion is the value of area specific resistance (ASR) must be ≤ 0.30 Ω cm\(^2\) at intermediate temperature of 500 °C - 800 °C [9]. Mixed ionic and electronic conductor (MIEC) materials such as lanthanum strontium cobaltite, La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_{3-δ}\) (LSC) is a common cathode material for O\(^2-\)-SOFC application [8,10,11].

The LSC material has also been used for H\(^+\)-SOFC application which uses doped-barium cerate-zirconate proton conductor materials such as BaZr\(_{0.1}\)Ce\(_{0.7}\)Y\(_{0.1}\)Yb\(_{0.1}\)O\(_{3-δ}\) (BCZYYb) and BaCe\(_{0.54}\)Zr\(_{0.36}\)Y\(_{0.1}\)O\(_{2.95}\) (BCZY) as reported by Wang et al. [12] and Abdul Samat et al. [13], respectively. The ASR values of the LSC cathode at 600 °C working with the BCZYYb was 1.78 Ω cm\(^2\) and the BCZY was 0.70 Ω cm\(^2\).

To achieve the targeted ASR value (≤ 0.30 Ω cm\(^2\)), Wang et al. [12] have developed a composite material of LSC-BCZYYb. The developed composite material recorded lower ASR value than the LSC at 600 °C which is 0.34 Ω cm\(^2\). The noteworthy result indicates that the composite material has better electrochemical properties than the MIEC material. Therefore, the development of LSC-BCZY composite material is expected to significantly reduce the ASR value of LSC cathode working with BCZY electrolyte material for intermediate temperature H\(^+\)-SOFC application. However, the properties of LSC-BCZY composite material such as phase purity and homogeneity need to be optimized first before any electrochemical performance testing can be done. The effect of different weight ratio percentage of LSC to BCZYYb on the properties of LSC-BCZY is systematically presented and discussed in this present work.

### 2 Materials and Methods

#### 2.1 Powder preparation

In-house developed La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_{3-δ}\) (LSC) and BaCe\(_{0.54}\)Zr\(_{0.36}\)Y\(_{0.1}\)O\(_{2.95}\) (BCZY) powders were used to prepare the LSC-BCZY composite powders. Based on citrate-EDTA sol gel method [14], LSC powder was synthesized using La(NO\(_3\))\(_3\).6H\(_2\)O, Sr(NO\(_3\))\(_2\) and Co(NO\(_3\))\(_3\).6H\(_2\)O as starting materials. A stoichiometric amount of the starting materials was dissolved in deionized water to form a metal nitrate salt precursor solution. Then, a stoichiometric amount of a combined chelating agent consisting of citric acid and ethylenediaminetetraacetic acid (EDTA) was added into the precursor solution. Then, the pH of the solution was adjusted to 0.5 by adding an appropriate amount of ammonium hydroxide solution and followed by adding a stoichiometric amount of ethylene glycol as polymerizing agent. The solution was heated at 150 °C for several hours to form a viscous gel the gel was dried at 250 °C for 5 hours to obtain as-synthesized black ash powder. Subsequently, the powder was calcined at 900 °C for 5 hours to obtain black fine powder.
In the similar method, BCZY powder was synthesized using \( \text{Ba(NO}_3\text{)}_2 \), \( \text{Ce(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \), \( \text{Zr(NO}_3\text{)}_2 \cdot \text{xH}_2\text{O} \) and \( \text{Y(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) as precursor materials. After adding the combined chelating agent, the pH of the solution was adjusted to 7. The obtained viscous gel was dried at 325 °C for 12 hours and the produced black ash powder was further calcined at 1100 °C for 10 hours to obtain yellowish fine powder. The details for the synthesis of BCZY powder was described elsewhere [15].

The LSC-BCZY composite powders were prepared via solid state mixing method. The calcined LSC and BCZY powders in different weight ratio percentage (wt%) of LSC to BCZY (LSC:BCZY) were grounded in an agate mortar for an hour. Then, the grounded mixture was dried in a drying oven for overnight. The produced LSC-BCZY composite powders were denoted as S1 (30:70), S2 (50:50) and S3 (70:30).

2.2 Powder characterization

To confirm the formation of LSC and BCZY perovskite phases in the prepared LSC-BCZY composite powders (S1, S2 and S3), the powders were subjected to X-ray diffractometry (XRD) analysis by using an XRD machine (Bruker, D8-Advance, Germany) within the 2θ range of 20° to 70°. The XRD analysis was done at room temperature by using Cu-Kα radiation source (\( \lambda = 0.1540558 \text{ nm} \)). A Brunauer-Emmett-Teller (BET) surface area and porosity analyzer (Micromeritics, ASAP 2020, USA) was used to analyze the BET-specific surface area. A Carl Zeiss SMT Supra-40VP scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer was used to capture the morphology image of the prepared composite powder. The image was captured in secondary electron mode using an accelerating voltage of 10 kV. The elemental composition analysis was performed by using the captured image of the prepared composite powder.

3 Results and discussion

Fig. 1 shows the XRD plots of the prepared LSC-BCZY composite powders (S1, S2 and S3). The crystalline peaks of LSC perovskite phase were matched with Joint Committee of Powder Diffraction Standards (JCPDS) file no. 48-0121 and the crystalline peaks of BCZY perovskite phase were matched with JCPDS file no. 89-2485. The results are in-line with the XRD plots of the pure in-house developed LSC and BCZY powders as reported elsewhere [14,15]. However, the XRD plots confirmed that all of the prepared composite powders did not form a pure composite phase of LSC-BCZY. It is due to the presence of impurity phases such as barium carbonate (\( \text{BaCO}_3 \), JCPDS file no. 52-1528) and strontium carbonate (\( \text{SrCO}_3 \), JCPDS file no. 05-0418) and the formation of peaks of other unknown impurity phases. The percentage of impurity phases (by considering the known peak only) in each of the prepared composite powder is calculated by using the following equation:

\[
\% I_m = I_m/(I_m + I_p) \times 100\% 
\]  

where \( I_m \) represents the maximum intensity of the impurity phase and \( I_p \) represents the maximum intensity of the perovskite phase. The results are tabulated in Table 1. S3 has the lowest percentage of impurity phases as compared to S1 and S2. From the table, it can be seen that the percentage of impurity phases decreased as wt% of LSC and BCZY in the prepared LSC-BCZY composite powders increased and decreased, respectively. The reason for this observation is still unclear since some of the peaks in the XRD plots could not be
identified yet. Further analysis and investigation on this observation is in progress and the results will be reported elsewhere.

Fig. 1. XRD plots of the prepared LSC-BCZY composite powders

Table 1. Percentage of perovskite and impurity phases in the prepared LSC-BCZY composite powder

| Powder   | LSC Perovskite phase (%) | LSC Impurity phase (%) | BCZY Perovskite phase (%) | BCZY Impurity phase (%) | Total impurity phase (%) |
|----------|--------------------------|------------------------|---------------------------|------------------------|-------------------------|
| S1 (30:70) | 72.11                    | 27.89                  | 46.70                     | 53.30                  | 81.19                   |
| S2 (50:50) | 78.96                    | 21.04                  | 48.13                     | 51.87                  | 72.91                   |
| S3 (70:30) | 81.16                    | 18.84                  | 49.44                     | 50.56                  | 69.40                   |

Ba and Sr are the two elements that easily react with carbon dioxide (CO₂) to form stable carbonate compounds. Formation of impurity phases of BaCO₃ and SrCO₃ is common in the preparation of powder through solid state mixing method or other methods including sol-gel, co-precipitation and hydrothermal [16–20]. The stable carbonate compounds usually require high calcination temperature (> 1300 °C) to decompose [19, 21,22]. However, high heat treatment lead to poor quality of the produced powders [23–25]. From the Table 1, it can be also clearly seen that the percentage of BaCO₃ is higher than the SrCO₃ in all composite powder. It might be contributed to a larger ionic radius of Ba than Sr, thus Ba reacts more towards CO₂ to form carbonate compound than the Sr. Further investigation on this observation is also in progress and the results will be reported elsewhere.

Typical SEM micrographs of the prepared composite powders (S1, S2 and S3) and their EDX spectra are shown in Fig. 2 and Fig. 3, respectively. All of the composite powders showed similar clump-like network structure. It can be clearly seen that the S1 is slightly more porous than the S2 and S3. It is supported by a larger value of BET-specific surface area for S1 (4.82 m² g⁻¹) than the S2 (3.58 m² g⁻¹) and S3 (3.48 m² g⁻¹). Comparing the three SEM micrographs, it was evident that the particle size of the produced composite powders prepared by solid state mixing method was small, but the particle size distribution was not
even due to the formation of agglomerated particles. The same observation was also reported by Chen et al. [26] in producing Pr$_2$NiO$_4$-Pr$_{0.2}$Ce$_{0.8}$O$_{1.9}$ composite powder for intermediate temperature SOFC application.

Fig. 2. SEM micrograph of the prepared LSC-BCZY composite powders

Fig. 3. EDX spectra of the prepared LSC-BCZY composite powders

The non-homogenous phase and particle size led to the non-homogeneous elemental composition in the prepared LSC-BCZY composite powders as shown in Table 2. Non-homogeneous elemental composition is another drawback of powders prepared by solid state mixing method [27,28]. From the table (Table 2), it can be seen that the calculated
elemental mole fractions of Co/Ba/Ce/Y in the prepared LSC-BCZY composites are close
to their nominal mole fractions. However, the calculated elemental mole fraction of Zr in
all of the prepared composite powders is deviated from its nominal mole fraction although
it is decreased as the wt% of BCZY decreased from 70% (S1) to 30% (S3) in the prepared
LSC-BCZY composite powders. It is due to the fact that Zr tends to form Zr-rich clusters as
previously reported by Osman et al. [29]. Consequently, the non-homogenize distribution
of Zr element in the prepared powders gave rise to the fluctuations of chemical
composition. The formation of Zr-rich clusters might have contributed to the deviations of
La/Sr mole fractions from their nominal mole fractions in all of the prepared composite
powders. The Zr-rich clusters might have covered these two elements from being fully
detected during EDX analysis as the analysis is done at a specific area or spot and
elemental distribution at an area is different from other areas [30].

Table 2. Elemental composition of the prepared LSC-BCZY composite powders

| Element | Nominal mole fraction | Calculated mole fraction |
|---------|-----------------------|--------------------------|
|         |                       | S1 | S2 | S3                 |
| La      | 0.60                  | 0.15| 0.13| 0.17               |
| Sr      | 0.40                  | 0.14| 0.10| 0.19               |
| Co      | 1.00                  | 1.00| 1.00| 1.00               |
| Ba      | 1.00                  | 1.00| 1.00| 1.00               |
| Ce      | 0.54                  | 0.55| 0.57| 0.56               |
| Zr      | 0.36                  | 1.16| 0.83| 0.77               |
| Y       | 0.10                  | 0.55| 0.63| 0.10               |

4 Conclusions

Composite powders of La_{0.6}Sr_{0.4}CoO_{3-δ}-BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (LSC-BCZY) with different
weight percentage (wt%) ratios of LSC to BCZY (LSC: BCZY = 30:70, 50:50 and 70:30)
were successfully prepared through solid state mixing method. However, the purity of the
prepared composite powders is quite low due to the formation of carbonate compounds
impurity including BaCO$_3$ and SrCO$_3$ and the presence of other unknown impurity phases.
All of the prepared composite powders have porous and clump-like network structures.
Furthermore, the powders tend to form Zr-rich clusters, resulting to the non-homogeneous
elemental composition distribution. Overall, S3 is better than the S1 and S2 since it has the
lowest percentage of impurity phases and the closest calculated mole fraction to the
nominal mole fraction of elemental composition. In order to yield a higher purity and better
elemental composition distribution of LSC-BCZY composite powder, further modification
of the preparation method is in progress and the outcomes will be reported elsewhere.
Later, a high purity and a homogeneous LSC-BCZY composite powder will be subjected to
the electrochemical performance testing for the application as cathode material in
intermediate temperature H$^+$-SOFC.

The authors would like to thank the School of Materials Engineering, Universiti Malaysia Perlis
(UmMAP), Universiti Teknologi MARA (UiTM) Perlis Branch and Centre for Research and
Instrumentation Management (CRIM) of Universiti Kebangsaan Malaysia (UKM) for the facility
support.
References

1. S. Hossain, A.M. Abdalla, S.N.B. Jamain, J.H. Zaini, A.K. Azad, Renew. Sustain. Energy Rev. 79, 750 (2017)
2. N.L.R.M. Rashid et al., Ceram. Int. 45, 6605 (2019)
3. N.A. Baharuddin, N.A. Mohd Nazrul Aman, A. Muchtar, M.R. Somalu, A. Abdul Samat, M.I. Aznam, Ceram. Int. 45, 12903 (2019)
4. A. Abdul Samat, W.N.A. Wan Yusoff, N.A. Baharuddin, M.R. Somalu, A. Muchtar, N. Osman, Process. Appl. Ceram. 12, 277 (2018)
5. M. Jafari, H. Salamati, M. Zhihan, E. Shahsavari, Int. J. Hydrog. Energy, 44, 1953 (2019)
6. R.A. Budiman et al., Solid State Ion. 332, 70–76 (2019)
7. D. Xie, K. Li, J. Yang, D. Yan, L. Jia, B. chi, J. Pu, J. Li, Int. J. Hydrog. Energy, In Press (2020) doi: 10.1016/j.ijhydene.2020.01.014.
8. O. Gwon, S. Yoo, J. Shin, G. Kim, Int. J. Hydrog. Energy, 39, 20806 (2014)
9. N.P. Brandon, S. Skinner, B.C.H. Steele, Annu. Rev. Mater. Res. 33, 183 (2003)
10. C. Benel, A.J. Darbandi, R. Djenadic, A. Evans, R. Tolke, M. Prestat, H. Hahn, J. Power Sources, 229, 258 (2013)
11. J. Hayd, L. Dieterle, U. Guntow, D. Gerthsenn, E. Ivers-Tiffée, J. Power Sources, 196, 7263 (2011)
12. M.S. Wang, J.X. Wang, C.R. He, Y.J. Xue, H. Miao, Q. Wang, W.G. Wang, Ceram. Int. 41, 5017 (2015)
13. A. Abdul Samat, M.R. Somalu, A. Muchtar, N. Osman, IOP Conf. Ser. Earth Environ. Sci. 268, 012136 (2019)
14. A. Abdul Samat, M.R. Somalu, A. Muchtar, O.H. Hassan, N. Osman, J. Sol-Gel Sci. Technol. 78, 382 (2016)
15. N.A. Abdullah, S. Hasan, N. Osman, J. Chem. 2013, 1 (2013)
16. S.V. Seyed-Vakili, C.R. Graves, A. Babaie, S. Heshmati-Manesh, M.B. Mogensen, Fuel Cells, 17, 108 (2017)
17. S. Zhuang, Y. Liu, S. Zeng, J. Lv, X. Chen, J. Zhang, J. Sol-Gel Sci. Technol. 77, 109 (2016)
18. R. Gawel, K. Przybylski, M. Viviani, Mater. Chem. Phys. 147, 804 (2014)
19. W. Acuña, J.F. Tellez, M.A. Macías, P. Roussel, S. Ricote, G.H. Gauthier, Solid State Sci. 71, 61 (2017)
20. A. Abdul Samat, W.N.A. Wan Yusoff, N.W. Norman, M.R. Somalu, N. Osman, J. Kejuruter. S1, 1, 49 (2018)
21. A. Chakraborty, A. Das Sharma, B. Maiti, H.S. Maiti, Mater. Lett. 57, 862 (2002)
22. N. Osman, I.A. Talib, H.A. Hamid, Sains Malays. 38, 103 (2009)
23. S.K. Durani, S. Naz, M. Mehmood, M. Nadeem, M. Siddique, J. Saudi Chem. Soc. 21, 899 (2017)
24. X.-Z. Fu, J.-L. Luo, A.R. Sanger, N. Luo, K.T. Chuang, J. Power Sources, 195, 2659 (2010)
25. A. Abdul Samat, S. Mohd Senari, M.R. Somalu, A. Muchtar, O.H. Hassan, N. Osman, Sains Malays. 47, 589 (2018)
26. X. Chen, J. Wang, Q. Liang, X. Sun, X. Zhu, D. Zhou, J. Meng, Solid State Sci. 100, 106108 (2020)
27. Z. Shao, W. Zhou, Z. Zhu, Prog. Mater. Sci. 57, 804 (2012)
28. A. VahidMohammadi, Z. Cheng, J. Electrochem. Soc. 162, F803 (2015)
29. N. Osman, I.A. Talib, H.A. Hamid, Sains Malays. 39, 479 (2010)
30. B. Choudhury, A. Choudhury, Curr. Appl. Phys. 13, 1025 (2013)