Influence of microstructure on the electrochemical behaviour of LSCF-SDCC

H.A. Rahman¹, K.H. Ng¹, S. Ahmad¹, H. Taib¹, S. Mahzan¹, S. M. Salleh¹, A. Ismail¹ and A. Muchtar²
¹Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Johor 86400, Malaysia
²Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor

E-mail: hamimah@uthm.edu.my

Abstract. The correlation of cathode microstructure with the electrochemical behavior of LSCF-SDCC has been studied. In this study, LSCF-SDCC composite cathode powders were prepared using ball milling and calcined at 700-900°C. Cathode pellets were fabricated using the calcined powders via uniaxial press and sintered at 600°C. A reduction of pellet porosity (33.1-29.8%) was observed as the calcination temperature increased, which was also in line with the cross-sectional view of the pellet. In electrochemical analysis, dominant resistance was observed in all samples which corresponded to low adsorption of oxygen. Meanwhile, cathode prepared with calcined powders of 750°C exhibited the least area specific resistance that yielded single cell performance of 139 mW/cm² at 550°C.

Keywords: composite cathode, LSCF-SDCC, calcination, solid oxide fuel cell

1. Introduction

Solid oxide fuel cells (SOFC) technologies offer cleaner, wide fuel choices and higher electrical efficiency over fossil fuel power generation system. In the past decade, substantial effort has been paid towards cell operated within intermediate to low temperature (400-800°C), with the aim to accelerate the cell commercialization and to achieve better cell stability and durability. However, reduction of temperature usually causes large cathodic polarization resistance that dramatically reduces the performance. Hence, a high catalytic cathode material is required to possess good electrochemical activity [1,2].

Lanthanum strontium cobalt ferrite oxide (LSCF) is considered a popular perovskite structured (ABO₃) materials due to its remarkable electrochemical properties of mixed ionic and electronic conduction (MIEC), high oxygen reduction rate and good chemical stability at IT-LT regime. Besides owning superior properties, pure LSCF is often reported with high cathodic polarization resistance due to conductivity that drops dramatically especially at low temperature [3,4]. Therefore, to enhance the electrochemically active reaction sites known as triple phase boundary (TPB), electrolyte materials
such as gadolinia doped ceria (GDC), samarium doped ceria (SDC) and samarium doped ceria carbonates (SDCC) are often added into LSCF; forming composite cathodes [5–8].

At low operating temperatures (400-600°C), SDCC is reported with better chemical and mechanical stabilities as well as better ionic conductivity compared to GDC and SDC, which lead to better cell performance [9, 10]. Besides that, calcination process would affect the powder properties of the composite cathode such as the surface area and particle size, and the microstructural aspect of the pellet [11]. Microstructure of the cathode is one of important factors which can influence the TPB area. It is believed that, this aspect significantly affects the electrochemical performance [12,13]. Taking both advantages of LSCF and SDCC into account, it is expected to yield an excellent composite cathode. However, it is interesting to understand the electrochemical behavior of this composite cathode with relation of calcination temperatures. In the present study, LSCF-SDCC composite cathode powders were prepared using high energy ball milling method at 550 rpm and calcined at 700-900°C. Later, the calcined powders were uniaxial pressed and sintered at 600°C. The influence of calcination temperature on the physical properties of composite cathode pellet was evaluated. In relation to that, the electrochemical and cell performance were evaluated using symmetrical and single cells respectively.

2. Experimental

A. Sample preparation

In this study, all chemicals were supplied from Sigma Aldrich (USA) with purity > 99.9%. The SDCC electrolyte powder was prepared using SDC with the carbonates (67 mol.% Li$_2$CO$_3$: 33 mol.% Na$_2$CO$_3$) at the weight ratio of 80:20 respectively. 50 wt.% LSCF was mixed with the prepared SDCC using wet ball milling method. The mixing was performed using a ball milling machine (Pulverisette 6, Fristch, Germany) at 550 rpm for 2 h in a zirconia jar. Afterward, the resultant wet mixture was dried and calcined at different temperatures (700, 750, 800, 850 and 900 °C) for 2 h [14]. Cathode pellets of 13 mm in diameter were fabricated using uniaxial compression.

Symmetrical cells (LSCF-SDCC/SDC/LSCF-SDCC) of about 1.4 mm in thickness were fabricated via co-pressing at 46 MPa and sintered at 600°C for 2 h. NiO-SDCC composite anode powder comprising of 60 wt.% NiO (Sigma Aldrich, USA) was prepared using ball milling at 150 rpm for 2 h, dried and calcined at 680 °C for 1 h. Later, the electrolyte supported single cell consisting of LSCF-SDCC/SDCC/NiO-SDCC was co-pressed and sintered at 600°C for 2 h. The amount of powder was controlled for each layer to achieve 0.40, 0.85 and 0.35 mm for cathode/electrolyte/anode respectively. The overall cross section is observed using scanning electron microscope as presented in Figure 1. The fabricated cell demonstrated crack and delamination free single cell.

![Figure 1. SEM micrograph of (a) fabricated LSCF-SDCC/SDCC/NiO-SDCC single cell (b) cathode-electrolyte interface (c) electrolyte-anode interface](image-url)
B. Characterisation and electrochemical measurements

The porosity of the cathode pellets was measured based on Archimedes principle. Ethanol was used as immersion medium to avoid solubility of carbonates [15]. The morphology of the cathode pellets was examined using scanning electron microscopy (SEM) (Jeol-Japan). An electrochemical workstation (Solatron, UK) was used to evaluate the cathode interfacial resistance via a symmetrical cell. The symmetrical cells were tested under AC amplitude of 10 mV and recorded from 0.1-100 kHz at 475-550°C in static air. Pt mesh was placed on both surfaces of the symmetrical cell as current collector. Meanwhile, the performance of the electrolyte supported cell was measured using a SOFC cell performance tester (Chino, Japan) at 475-550°C. Silver paste was applied on both anode and cathode sides of the cell as current collector (RS Components, UK). Purified hydrogen and oxygen were used as fuel and oxidant at the flow rate of 60 mL/min and 100 mL/min respectively.

3. Result and Discussions

A. Microstructural and physical analysis

A cathode component of SOFC requires good amount of porosity for oxygen diffusion and transfer to the cathode-electrolyte interface. In this study, cathode pellets were fabricated from calcined powders of 700-900°C that were subsequently sintered at 600°C. The porosity result of LSCF-SDCC obtained via Archimedes method is presented in Figure 2. Slight reduction of porosity can be observed at increasing calcination temperature from 33.1% at 700°C to 29.8% at 900°C. The monotonous reduction of the pellet porosity might be attributed to increment of particle size of LSCF-SDCC powder at increased calcination temperatures. Particle necking process was probably promoted at high calcination temperatures that normally tend to form agglomerates and eventually reduces the porosity of the pellets [16, 17].

![Figure 2. Porosity of LSCF-SDC carbonate pellets fabricated from various calcined powders](image)

Figure 3 shows the cross-sectional SEM micrographs of cathode pellets obtained in back scattered electron mode (BSE). In BSE imaging, dark region represents the pores of the pellet and the bright region corresponds to the phases of LSCF and SDCC. Cathode pellets prepared from powder calcined at 900°C revealed the least dark region as compared to 700°C, which indicates decreasing porosity at increasing calcination temperatures. This finding is in good agreement with the porosity results. Meanwhile, all samples demonstrated good amount of porosity (20-40%) that had fulfilled the requirement as cathode.
**Figure 3.** Cross sectional SEM micrograph for LSCF-SDC carbonate pellets prepared from powders calcined at various temperatures

**B. Electrochemical performance**

Figure 4 shows impedance spectra of the samples tested at 475-550°C with an increasing interval of 25°C. Figure 5 presents the equivalent circuit consisting of $R_{ohm}(R1CPE1)-(R2CPE2)$ that was used for impedance data fitting. $R_{ohm}$ corresponds to intersection of high frequency arc on the real axis ($Z'$), whereby the resistance is contributed from electrolyte resistance, current collector and connecting wire. Meanwhile, $R1$ corresponds to the resistance attributed to oxygen ($O_2$) charge transfer processes at high to medium frequency, and $R2$ represents the resistance due to $O_2$ species adsorption and diffusion at low frequency. The total polarization resistance ($R_p$) is the sum of $R1$ and $R2$, which is represented by high to low frequency intercepts [18].
Figure 4. Impedance spectra of LSCF-SDC carbonate symmetrical cells at 475-550°C operating temperature

![Impedance Spectra](image)

Figure 5. Equivalent circuit used for impedance data fitting

The equivalent circuit model fit the data set with chi-square in the range of 1-2 x 10^{-4}. Based on the impedance data fitting, the impedance spectra shows reduction of $R_{\text{ohm}}$ and the total electrode polarization resistance, $R_p = (R_1+R_2)$ when the working temperature increases. This can be clearly evidenced on the reduction of arc size. The total resistance ($R_p$) for all samples are mainly contributed from $R_2$ that is due to considerably low adsorption and dissociation of $O_2$. Such finding also suggests that the predominating cathodic process was mostly associated to charge transfer process due to smaller $R_1$ arcs observed [19]. The contribution of $R_2$ might be caused by (1) increment of particle size and (2) reduction of porosity. In this study, the increment of particle size attributed to increasing calcination temperatures may potentially lead to reduction of TPB as electrochemically active sites [1]. The increase in $R_2$ might be also associated with lesser pore size and porosity level at increasing calcination temperature as observed in Figure 2. The decrease in porosity may lead to current constriction, and thereby increased the cathode-electrolyte interfacial resistance [20].
The area specific resistance (ASR) values were obtained using the total polarization resistance (Rp), multiplied with an active surface area of the cathode. The clear linear relationship between the ASR and operating temperature are presented in Figure 6, as a function of log (ASR) against 1000/T. Arrhenius equation was applied to evaluate the activation energy based on the plot. It can be evidently observed from the increasing ASR value from 0.35 to 0.54 $\Omega$cm$^2$ at operating temperature 475–550°C for LSCF-SDCC calcined at 750°C. The ASR values are within the range with other LSCF composite cathode system reported in the literature (0.31–0.69 $\Omega$cm$^2$) [7,21–23]. LSCF-SDCC calcined at 750°C was found with the least ASR value and activation energy of 0.35 $\Omega$cm$^2$ and 0.65 eV respectively, at operating temperature of 550°C.

![Figure 6. Area specific resistance of LSCF-SDCC calcined from 700 to 900°C](image)

**C. Cell performance**

The single cells consisting of LSCF-SDCC/SDCC/NiO-SDCC were fabricated using uniaxial press and co-sintered at 600°C. Air was used in cathode as oxidant and hydrogen as fuel in anode respectively. Figure 7 represents the current-voltage-power density (I-V-P) curves of calcined LSCF-SDCC tested at 475-550°C. Better cell performance was observed at increased operating temperature, specifically at 550°C. Such finding might be due to the effect of transition temperature slightly above the melting point of the carbonate (~ 500°C). This occurrence has been also reported by several authors with carbonate based electrolytes. It is believed that, the melting of the carbonates assisted the multi-ionic conduction paths (H+, O$^{2-}$ and CO$_{3}^{3-}$) and charge transfer mechanism which had improved the cell performance [9,24,25].

Based on the I-V-P curves, as expected that the LSCF-SDCC powder calcined at 750°C demonstrated better cell performance of 139.91 mW/cm$^2$ operated at 550°C compared to other samples. Lower maximum power density was obtained for LSCF-SDCC calcined at 800, 850 and 900 °C, with maximum powder densities of 84.11, 73.74 and 77.83 C mW/cm$^2$ respectively. The effects of larger particle size and reduction of porosity attributed to increasing calcination temperatures might had affected the TPB region. The performance results are also in good agreement with the increase in total R$_p$ and ASR as discussed earlier. Nonetheless, the present finding is still comparable with other composite cathodes with the usage of carbonate based electrolyte such as 92 mW/cm$^2$ [26] and 155 mW/cm$^2$ [27]. Although the finding is on a par with those of several authors, the interfacial resistance and ASR are considerable high. For further improvement on the interfacial resistance and ASR, there
are still various factors to be optimized. It is interesting to note that, these factors are important to be studied such as the cell design by adopting anode supported design, cell fabrication techniques, and cell operating parameters such as the fuel rates.

Figure 7. Cell performance of LSCF-SDCC single cell fabricated from calcined powders of (a) 700°C (b) 750°C (c) 800°C (d) 850°C and (e) 900°C

4. Conclusions
In this study, LSCF-SDCC composite cathode pellets were fabricated from calcined powders (700-900°C) and sintered at 600°C. The effects of calcination temperatures were studied based on the porosity, electrochemical behavior and the cell performance. The porosity of the pellets demonstrated good amount of porosity (20-40%); although the porosity level reduced with the increase of
calcination temperatures. Decrement of porosity was suspected to affect the electrochemical as well. Based on the electrochemical performance, calcined powders at 750°C yielded the lowest ASR of 0.35 Ωcm² and the highest cell performance of 139.91 mW/cm² when operated at 550°C.

Acknowledgment
The authors gratefully acknowledge the financial supports from the Universiti Tun Hussein Onn Malaysia (UTHM) and the research funds from Ministry of Higher Education (FRGS, Vot 1541).

References
[1] Huang, X., Shin, T.H., Zhou, J. and Irvine, J.T. 2015. Hierarchically nanoporous La$_{1.7}$Ca$_{0.3}$CuO$_{4-δ}$ and La$_{1.7}$Ca$_{0.3}$Ni$_{0.5}$Cu$_{0.5}$O$_{4-δ}$ (0.25 ≤ x ≤ 0.75) as potential cathode materials for IT-SOFCs. Journal of Materials Chemistry A, 3(25) pp 13468-13475.
[2] Kilner, J.A. and Burriel, M. 2014. Materials for intermediate-temperature solid-oxide fuel cells, Annual Review of Materials Research,  44 pp 365-393.
[3] Rembelski, D. Viricelle, J.P., Combemale, L. and Rieu, M. 2012. Characterization and comparison of different cathode materials for SC-SOFC: LSM, BSCF, SSC, and LSCF. Fuel Cells 12(2) pp. 256-264.
[4] Han, G.D. 2016. Fabrication of lanthanum strontium cobalt ferrite (LSCF) cathodes for high performance solid oxide fuel cells using a low price commercial inkjet printer. Journal of Power Sources 306 pp 503-509.
[5] Zhao, V. 2014. Stability of nanorod-structured La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3−δ}$–Gd$_{0.3}$Ca$_{0.7}$O$_{1.9}$ composite cathodes for intermediate temperature solid oxide fuel cells. Ceramics International 40(9) pp 14891-14898.
[6] Leng, Y., Chan, S.H. and Liu, Q. 2008. Development of LSCF–GDC composite cathodes for low-temperature solid oxide fuel cells with thin film GDC electrolyte. International Journal of Hydrogen Energy 33(14) pp 3808-3817.
[7] Baharuddin, N.A., Muchtar, A., Somalu, M.R., and Rahman, H.A. 2016. Influence of sintering temperature on the polarization resistance of La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3−δ}$–SDC carbonate composite cathode. Ceramics–Silikáty 60(2) pp 115-121.
[8] Shen, F. and Lu, K. 2015. La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3}$ cathodes incorporated with Sm0. 2Ce0. 8O2 by three different methods for solid oxide fuel cells. Journal of Power Sources 296 pp 318-326.
[9] Chen, M., Zhang, H., Fan, L., Wang, C. and Zhu, B. 2014. Ceria-carbonate composite for low temperature solid oxide fuel cell: Sintering aid and composite effect. International journal of hydrogen energy 39(23) pp 12309-12316.
[10] Zhu, B., Fan, L. and Lund, P. 2013. Breakthrough fuel cell technology using ceria-based multi-functional nanocomposites. Applied energy 106 pp 163-175.
[11] Liu, P., Kong, J., Liu, Q., Yang, X. and Chen, S. 2014. Relationship between powder structure and electrochemical performance of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3−δ}$ cathode material. Journal of Solid State Electrochemistry 18(6) pp 1513-1517.
[12] Ng, K.H., Lidiyawati, S., Somalu, M.R., Muchtar, A. and Rahman, H.A. 2016. Influence of Calcination on the Properties of Nickel Oxide-Samarium Doped Ceria Carbonate (NiO-SDCC) Composite Anodes. Procedia Chemistry 19 pp 267-274.
[13] Kim, Y.M., Baek, S.W. Bae, J. and Yoo, Y.S. 2011. Effect of calcination temperature on electrochemical properties of cathodes for solid oxide fuel cells. Solid State Ionics 192(1) pp 595-598.
[14] Rahman, H.A., Muchtar, A., Muhamad, N. and Abdullah, H. 2012. Structure and thermal properties of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3−δ}$–SDC carbonate composite cathodes for intermediate-to low-temperature solid oxide fuel cells. Ceramics International 38(2) pp 1571-1576.
[15] Jarot, R., Muchtar, A., Wan Daud, W.R., Muhamad, N. and Majlan, E.H. 2011. Porous NiO-SDC carbonates composite anode for LT-SOFC applications produced by pressureless sintering. In Applied Mechanics and Materials 52 pp 488-493.
[16] da Conceicao, L., Silva, A.M., Ribeiro, N.F. and Souza, M.M. 2011. Combustion synthesis of La0.7Sr0.3Co0.4Fe0.5O3 (LSCF) porous materials for application as cathode in IT-SOFC. *Materials Research Bulletin* **46**(2) pp 308-314.

[17] Rahaman, M.N. 2003. *Ceramic Processing and Sintering*. Johor: CRC press.

[18] Zhou, Q., Guo, Y., Wang, F. 2013. Novel cobalt-free cathode material (Nd0.6La0.4)(Ni=Cu0.2Al0.03)O2 for intermediate-temperature solid oxide fuel cells. *Ceramic International* **41** pp 639.

[19] Zhou, W., Ran, R., Shao, Z., Cai, R., Jin, W., Xu, N. and Ahn, J. 2008. Electrochemical performance of silver-modified Ba0.5Sr0.5Co0.8Fe0.2O3 cathodes prepared via electroless deposition. *Electrochimica Acta* **53**(13) pp 4370-4380.

[20] Jørgensen, M.J., Primdahl, S., Bagger, C. and Mogensen, M.. 2001. Effect of sintering temperature on microstructure and performance of LSM–YSZ composite cathodes. *Solid State Ionics* **139**(1-2) pp 1-11.

[21] Xi, X., Abe, H. and Naito, M.. 2014. Effect of composition on microstructure and polarization resistance of solid oxide fuel cell anode Ni–YSZ composites by co-precipitation. *Ceramics International* **40**(10) pp 16549-16555.

[22] Nie, L., Liu, M., Zhang, Y. and Liu, M. 2010. La0.6Sr0.4Co0.3Fe0.5O3 cathodes infiltrated with samarium-doped cerium oxide for solid oxide fuel cells. *Journal of Power Sources* **195**(15) pp 4704-4708.

[23] Zhou, Q., Xu, L., Guo, Y., Jia, D., Li, Y. and Wei, W.C.J. 2012. La0.6Sr0.4Fe0.1Cu0.2O1.5 perovskite oxide as cathode for IT-SOFC. *International Journal of Hydrogen Energy* **37**(16) pp 11963-11968.

[24] Hei, Y., Huang, J., Wang, C. and Mao, Z. 2011. Novel doped barium cerate–carbonate composite electrolyte material for low temperature solid oxide fuel cells. *International Journal of Hydrogen Energy* **39**(26) pp 14328-14333.

[25] Xie, F., Wang, C., Mao, Z. and Zhan, Z. 2013. Preparation and characterization of La0.9Sr0.1Mg0.85–(LiNa)0.15O2 composite electrolytes. *International Journal of Hydrogen Energy* **38**(25) pp 11085-11089.

[26] Chockalingam, R. and Basu, S. 2011. Impedance spectroscopy studies of Gd–CeO2–(LiNa)CO3 nano composite electrolytes for low temperature SOFC applications. *International Journal of Hydrogen Energy* **36**(22) pp 14977-14983.

[27] Zhao, Y., He, Y., Fan, L., He, J., Xiong, D.B., Gao, F. and Zhu, B.. 2014. Synthesis of hierarchically porous LiNiCuZn-oxide and its electrochemical performance for low-temperature fuel cells. *International Journal of Hydrogen Energy* **39**(23) pp 12317-12322.