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Development of LSCF cathode perovskites for solid oxide fuel cell

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Abstract

Solid oxide fuel cell (SOFC) is a technology that converts chemical energy to electrical energy which is used to generate powers such as turbines. The cathode in SOFC is developed with the material consisting of lanthanum strontium cobalt ferrite (LSCF) with good mixed ionic electronic conductivity (MIEC) properties. The LSCF pellet is prepared by an annealing temperature in a furnace within the temperature of 600 to 900 ℃. With these temperatures, it is crucial to investigate the annealing temperature effect of the LSCF crystalline structure, morphological studies, and its electrical conductivity. The pellet contains LSCF undergoes X-ray diffraction (XRD) for crystalline structure and electrical impedance spectroscopy (EIS) for electrical performances and conductivity. The crystalline structure tested with XRD shows a similar diffraction peak even with the increasing temperature of annealing. As the annealing temperature gets higher, the main peak becomes smoother. As for the lowest annealing temperature of 600 ℃, the diffraction peaks seem unstable compared to 700 ℃ and above. This suggests that LSCF has a stability of structure at a high operating temperature of SOFC. The electrical impedance of the fabricated LSCF pellet is at the lowest annealing temperature of 600 ℃ with a value of 0.00554 Ω·cm. By the objective to lower the operating temperature of SOFC, the LSCF produces a small impedance and electrical conductivity. Also, the LSCF compound has the best structure stability at a high temperature above 700 ℃.

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1.0 Introduction

For years, solid oxide fuel cell (SOFC) devices convert chemical energy to electrical energy in power generation while producing very low greenhouse emissions. Rather than using combustion-based power generation such as coal, SOFC can produce lower SO_x and NO_x to the environment (Lassman, 2011). It contains a porous anode, electrolyte membrane, and porous cathode. This study focuses on the development of porous cathode as oxygen reduction reaction (ORR) reaction happens. For the cathode, it is important to fulfil the three main characterisations when it comes to ORR, which are high mixed ion-electron conductors (MIEC) properties, good structural ability, and high electrochemical properties for ORR. For this study, the cathode is produced by using LSCF as the main component, as LSCF has good MIEC properties (Han et al., 2017). Typically, the SOFC cathode is made up of lanthanum-based material such as lanthanum strontium manganate (LSM) and SOFC operates in high operating temperatures above 700–1000 ℃ so that it has higher conversion of chemical energy to electrical energy (Asadi et al., 2012). Unfortunately, these high temperatures contribute to inter-diffusion between cell material, sealing problems, and degradation of materials (Rembelski et al., 2012). Therefore, throughout this study, the LSCF component is being fabricated in the form of a pellet and investigated based on its morphology, microstructure, and electrical conductivity precisely at a lower operating temperature below 700 ℃. In a solid oxide fuel cell, it is important to have microstructure stability of the cathode component since it is the active site for ORR to happen.

2.0 Methodology

2.1 Fabrication of LSCF powder

Lanthanum strontium cobalt ferrite (LSCF) powder is mixed with starch and polyethylene glycol 200 which act as a binder. This mixture is then pressed using a 25 tonnes compression machine to form a 10 mm diameter and 2 mm thickness of pellet. The pellet is sintered in a furnace from the temperature of 600 to 900 °C. Then, the LSCF pellet is left to be cooled and characterised for lattice parameters, crystalline structure, and electrical conductivity.

2.2 Sample Characterisation

2.2.1 Lattice Parameter and Crystalline Structure

X-Ray Diffraction was performed by using X'Pert Pro MPD (Malvern PANalytical) with Cu Kα radiation of 40 kV, 20° < 2θ < 90° and a step size of 0.02°. The profile from the XRD pattern is used to determine the lattice parameter and the crystalline structure of LSCF.

2.2.2 Electrical Conductivity

To measure the electrical conductivity, Electrical Impedance Spectroscopy (EIS) is used by measuring the electrical impedance from imaginary impedance, Zi to real impedance, Zr. Measurement was done by utilizing an Impedance Analyzer (HIOKI). Impedance is the result of the frequency of the voltage to the current. The EIS data collected in the form of pellets within the temperature 25, 50, 60, 70, 80, 90, and 100 °C at 10 °C increment. The amplitude of measuring was 1.00 V in an open circuit voltage (OCV) mode.

3.0 Results and discussion

3.1 Effect of annealing temperatures towards the crystalline structure

The LSCF in powder form is annealed in furnaces ranging from temperature 600 to 900 °C. The LSCF powder was placed on a round metal disk, about 10 g.

Based on Fig. 1 and Fig. 2, as the annealing temperature increases, the main peaks for LSCF show higher intensity value which indicates high crystallinity at higher temperature. The diffraction planes for the main peak of LSCF powder remains at 2θ = 32° at every temperature. To have a good cathode electrode for a solid oxide fuel cell, it is important to have stability on the chemical and dimensional structure (Singhal, 2007). In comparison to the crystalline structure by temperatures, it clearly shows from the figures that XRD peaks for LSCF at 600 and 700 °C exhibits peak noise at its diffraction planes with low intensity which may attributed to impurity phases in its structure. LSCF shows no impurity phases of crystalline structure at annealing temperatures of 800 and 900 °C, which indicates good structure stability at higher annealing temperatures. This is corroborated with Choi et. al (2011) investigation on

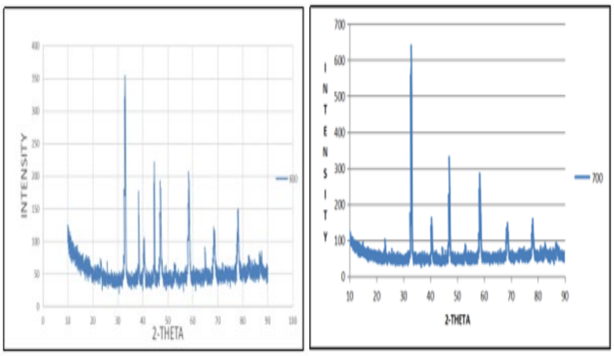


Fig. 1: Diffraction peak for 600 and 700°C

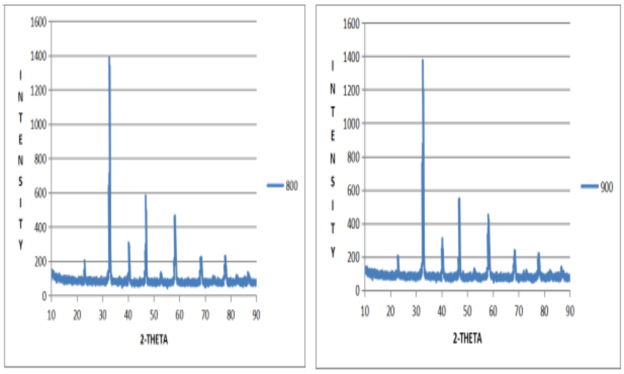


Fig. 2: Diffraction peak for 800 and 900 °C

chemical and micro-structural stabilities of LSCF annealed at 850 °C for 9 hours. It was found that the surface of the LSCF at high local contrast over the scale within each grain. This finding indicates that the bare LSCF is unstable for a long period of its operation. Therefore, fabricated LSCF coated with LSM and annealed for 9 hours at the same temperature of 850 °C showed better stability than the bare LSCF (Choi et al., 2011).

In another research by Venezia et al. (2019), LSCF is also ink-jetted with gadolinium doped ceria (CGO) ink which acts as an ionic conductor precursor. The study found that LSCF infiltrated CGO did not find any detectable structural differences between bare LSCF at cathode site. In another study by Xin et al. (2019), the LSCF with $Mn_{0.9}Y_{0.1}Co_2O_4$ (MYC) addition showed no impurity phases which proved to be good chemical stability. The same finding was obtained from other studies on the structure of LSCF coated with a dense electrolyte such as (CGO) which displayed stable and smooth grain growth from the behaviour of its diffraction planes (Lassman, 2011).

Fig. 3 shows the comparison of LSCF peaks at different diffraction plane at different annealing temperatures. The main peak of LSCF was identified at diffraction plane of 2θ = 32°.With increasing annealing temperature, the peak value was maintained but the

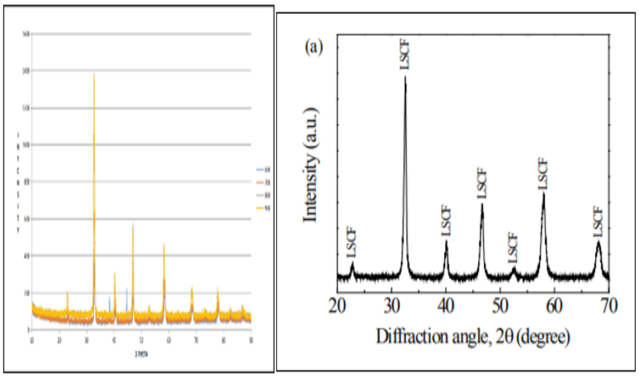


Fig. 3: Diffraction peak for 600, 700, 800 and 900°C

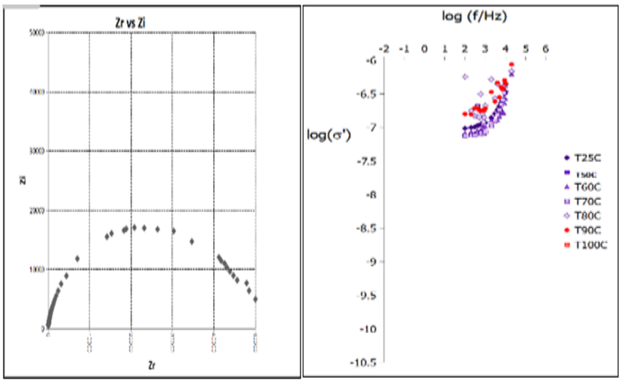
intensity value shows increment. The sharp peak represents the crystalline structure of each compound in LSCF (Yu et al., 2016). It is also a very distinct difference to be compared with bare LSM crystalline structure, where the peak also appeared at 2θ = 32.5° (Choi et al., 2011). Specifically, lanthanum manganite ($LaMnO_3$) based compound shows a diffraction peak located at 2θ = 32°. The XRD pattern of diffraction shows a difference in peak intensity even with the increasing annealing temperature of LSCF. This agrees with Akbari et al. (2015) who studied the calcined LSCF nano-powders at different temperatures, the crystallite size of LSCF increased as the calcination temperature increased.

3.2 Electrical conductivity at different annealing temperatures

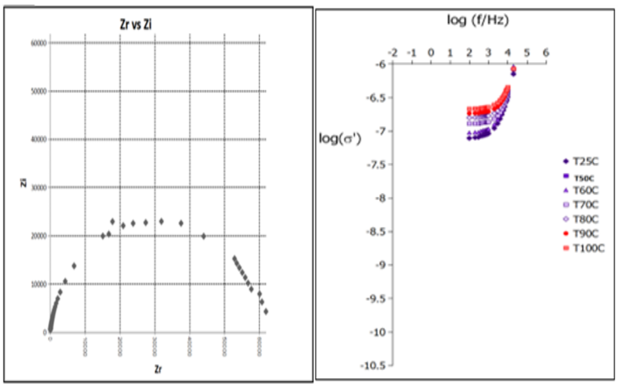
This impedance spectra curve was recorded in OCV mode from the temperature 25 to 100 °C, with a step size of 10 °C in a chamber while neglecting the humidity concerns. In the chamber, it was supplied by a high frequency of 1MHz to provide clear differences of polarisation curves (Marinha et al., 2011). The curve obtained shows the impedance of Zr vs Zi. This valuable data of impedance can be plotted into a polarisation resistance versus frequency

The highest electrical conductivity reading is produced from the LSCF-600 pellet with a value of 0.00554 Ω·cm. For LSCF-700, the highest value is recorded as 0.00127 Ω·cm. Meanwhile, for LSCF-800 the highest value of electrical conductivity is 0.00112 Ω·cm and for LSCF-900, the highest value is 0.00114 cm. By the research of Venezia et al. (2019), instead of pure LSCF, the LSCF was infiltrated with LSC, an MIEC precursor.

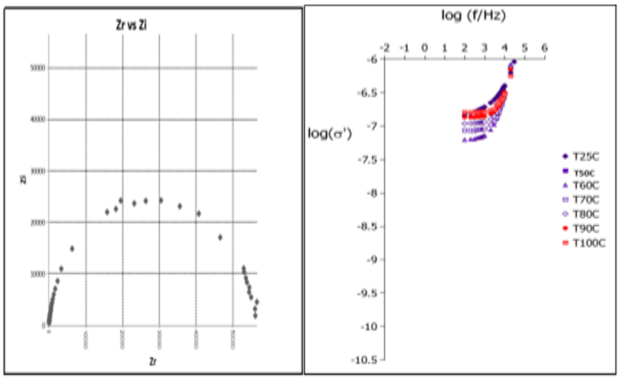
The finding shows a significant deterioration for the pure LSCF pellet due to low-frequency losses. The ohmic impedance of infiltrated LSC shows a resistance



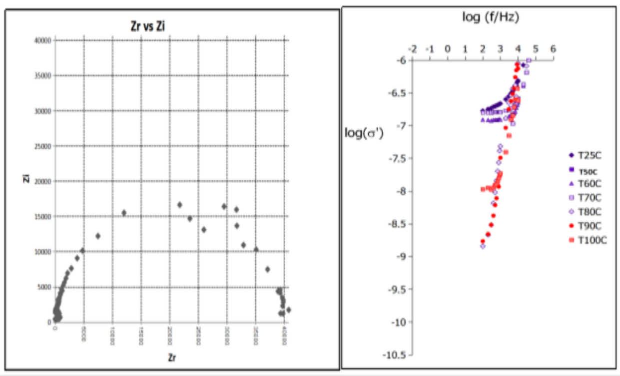
(a)



(b)



(c)



(d)

Fig. 4: (a) Impedance spectra reading for LSCF that has been annealing at temperature 600 °C (LSCF-600); (b) impedance spectra reading for LSCF annealed at temperature 700 °C (LSCF-700); (c) impedance spectra reading for LSCF annealed at temperature 800 °C (LSCF-800); and (d) impedance spectra reading for LSCF annealed at temperature 900 °C (LSCF-900)

value of 250 mW/cm^2. Venezia et al. (2019) noted that infiltrated cathode increases the catalytic activity and increases the ionic conductivity due to the contribution of LSC phases. This work coated with LSC increases the impedance by 250 mW/cm^2 compared to pure LSCF at the highest recorded at 0.00554 Ω·cm by this paper and method of annealing.

Among these four LSCF pellets, the LSCF-600 shows a significant value of electrical impedance. Theoretically, a high annealing temperature produces a high electrical impedance to a certain point. The results from EIS characterisation show that even at the lower range of high annealing temperature produces high electrical impedance. The effect of annealing temperature correlates to the discussion in Marika et.al work that too high annealing temperature leads to a loss of purity and subsequently decreases electrochemical performance (Letilly et al., 2012).

Different methods of fabricating LSCF cathode could be the cause of the difference in electrical conductivity (Lubini et al., 2016). In comparison, Lubini's conductivity of thermally treated LSCF is 100 times lower than the sintered LSCF due to extensive grain boundaries and the small size of crystalline structures that appear with extra heating.

Coating or pairing LSCF with another compound may cause a difference in polarisation resistance. This was observed in comparison to the Finklea study, where the LSCF was deposited on yttria-stabilised zirconia (YSZ). It shows a small polarisation resistance of 0.1 Ω·cm whereas the bare sintered LSCF holds a lower value of polarisation resistance of 0.005542 Ω·cm.

4.0 Conclusion

In conclusion, the fabrication of the LCSF is successfully fabricated by the annealing method after the LSCF is mixed with starch and polyethylene glycol as a binder. The annealing method varies from 600 to 900 °C. From the XRD pattern profile, it can be concluded that the intensity value changes with changes of annealing temperature. The main peak value remains at the same 2θ. The electrical conductivities decrease as the annealing temperature increases. However, compared to other results, bare LSCF conductivities are very different with mixed/coated LSCF. The conductivities of coated LSCF show a significant impedance of more than 0.0055 Ω·cm. Between the four annealing temperatures, the LSCF micro-structure is stable at high temperatures by the result of diffraction peaks. Once the microstructure of the component is stable, it could produce a good electrical conductivity certain period of time.

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