

Effects of Binary (Lithium/Natrium)₂ Carbonates on the Phase and Microstructural Stability of Lscf-Sdc for Low Temperature Solid Oxide Fuel Cells

(Kesan Karbonat (Litium/Natrium)₂ Bineri pada Fasa dan Kestabilan Mikrostruktur Lscf-Sdc untuk Bahan Api Sel Oksida Pepejal Bersuhu Rendah)

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ABSTRACT

Most studies focus on introducing of doped ceria carbonate into cathode materials to enhance the cathode ionic conductivity for low temperature solid oxide fuel cell. In this work, we aim to identify the influence of Lithium/Natrium binaries (Li/Na)₂ carbonates addition on Lanthanum Strontium Carbonate Ferrite-Samarium-Doped Ceria (LSCF-SDC) composite cathode on the phase and microstructural stability under long-term durability of 1000 h. Three different binaries (Li/Na)₂ carbonate of 67:33, 62:38, and 53:47 mol.% were incorporated into LSCF-SDC via high energy ball milling method. The phase and microstructural stability as a function of operating temperature (400 and 600 °C) were studied using X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). Archimedes principle was applied to evaluate the porosity of the cathode pellets. Electrochemical impedance spectroscopy measurements were performed by using impedance setup at 600 °C under open-circuit condition. The XRD findings demonstrated that cathodes able to retain their chemical phases after stability test. Qualitative results show that the cathode morphology exhibits a slight increment on the particle size after the ageing process at 1000 h. All cathodes prepared at various binary carbonate ratio still maintain their porosity values between 26 and 32% after long-term stability test. This finding has yielded a smaller area specific resistance of 0.66 Ω.cm² at 600 °C. Therefore, incorporating binary (Li/Na)₂ carbonate in LSCF-SDC shows a good combination when insignificant changes observed after long-term stability test of 1000 h.

Keywords: Binary carbonate; composite cathode; durability; impedances; LT-SOFC

ABSTRAK

Kebanyakan kajian fokus dalam memperkenalkan karbonat seria terdop ke dalam bahan katod untuk meningkatkan kekonduksian ionik bagi sel bateri oksida pepejal bersuhu rendah. Kajian ini bertujuan untuk mengenal pasti pengaruh penambahan karbonat Litium/Natirum (Li/Na)₂ bineri pada katod komposit Lantanum Strontium Kobalt Ferit-Samarium terdop Seria (LSCF-SDC) terhadap kestabilan fasa dan mikrostrukturnya di bawah ujian ketahanan berjangka panjang selama 1000 jam. Tiga nisbah karbonat (Li/Na)₂ bineri yang berbeza iaitu 67:33, 62:38, dan 53:47 %mol dicampurkan ke dalam LSCF-SDC menggunakan kaedah pengisaran bebola halaju tinggi. Kestabilan fasa dan mikrostruktur pada suhu operasi (400 dan 600 °C) dikaji menggunakan pembelauan sinar-X (XRD) dan mikroskop medan pancaran imbasan elektron (FESEM). Prinsip Archimedes diaplikasikan untuk mengukur keporosan pelet katod. Pengukuran spektroskopi impedans elektrokimia dilakukan dengan menggunakan persediaan impedans pada 600 °C di bawah keadaan litar terbuka. Hasil XRD membuktikan katod komposit mampu mengekalkan fasa kimianya selepas ujian kestabilan. Keputusan kualitatif morfologi katod menunjukkan sedikit peningkatan dalam saiz zarah selepas 1000 jam proses penuaan. Kesemua katod yang dihasilkan pada nisbah karbonat bineri yang berbeza masih mengekalkan nilai keliangan antara 26 hingga 32% selepas ujian kestabilan berjangka panjang. Hasil kajian memberikan nilai rintangan luas tentu yang rendah iaitu 0.66 Ω.cm² pada 600 °C. Oleh itu, penambahan karbonat (Li/Na)₂ bineri pada LSCF-SDCC menunjukkan kombinasi yang baik apabila tiada perubahan ketara diperhatikan selepas 100 jam ujian kestabilan berjangka panjang.

Kata kunci: Bineri karbonat; impedans; katod komposit; ketahanan; LT-SOFC

INTRODUCTION

Solid oxide fuel cells (SOFCs) technology has been considered as promising substitutes for conventional energy generation system due to their highly efficient-direct energy conversion, broad fuel choices and low emission of harmful gasses. Classical SOFCs requires high operating temperatures (~ 1000 °C), and that consequent in various technical challenges such as high material degradation rates, low cell durability, and high fabrication cost (Abdul Samat et al. 2016; Agun et al. 2014; Ahmad et al. 2012). To address these challenges, development of intermediate-low-temperature SOFCs (IT-LTSOFCs), ranging from 400-800 °C would bring significant benefits such as better lifetime of components, shorter startup cycles, less expensive component and fabrication cost, in order maintain the commercialization sustainability of SOFCs (Anwar et al. 2017).

Nevertheless, operating at IT-LT region remains a challenge, whereby the cell performance is largely affected by the slow kinetics of cathodes which limiting the oxygen reduction processes. Therefore, over the past decade, continues effort has been made on the development of high catalytic cathodes with reduced temperature. Perovskite structured materials (ABO_3) such as, Lanthanum Strontium Cobalt Ferrite Oxide (LSCF) have received significant research attention for its mixed-ionic-electronic-conduction, great electrochemical properties, high oxygen reduction rate reported at IT region (Asgar et al. 2017; Baharuddin et al. 2013). Great chemical compatibilities of LSCF with addition of ceria-based electrolytes to form composite cathode have been widely reported, such as gadolinium-doped ceria (GDC), samarium-doped ceria (SDC), and samarium-doped ceria carbonate (SDCc) (Ahmad et al. 2012; Baharuddin et al. 2017; Bu et al. 2016; Choi et al. 2017).

Among these electrolytes mentioned, extensive studies regarding SDCc electrolyte have demonstrated higher ionic conductivity due to presence of carbonate as secondary phase, such as binary $(Li/Na)_2$ carbonate. The carbonates provides multi-polar-ionic-conductions (O^{2-} , H^+ and CO_3^{2-}) that offer fast ionic path for charge transfer at low temperature regime (<600 °C) (Chen et al. 2014; Di et al. 2010; Raza et al. 2020). The melting of binary $(Li/Na)_2$ carbonate is the key factor forming the continuous molten phase that shorten the ionic paths for enhanced performance at low temperature. Therefore, the operational temperature must be slightly above the eutectic melting points of the carbonates. Different binary molar ratios of the $(Li/Na)_2$ carbonates can be used to tailor a lower eutectic melting point, which has been widely explored in optimizing the SDCc electrolyte (Dos Santos-Gómez et al. 2018; Fan et al. 2017).

On top of that, several studies has applied LSCF-SDCc composite cathode in single cell at low temperature region: 120.4 mW/cm² (Giuliano et al. 2017), 800 mW/cm² (Ghouse et al. 2010), and 1100 mW/cm² (Di et al. 2010), at 550 °C, respectively. Although moderate power densities were reported, however, no studies have been conducted with the relation of various binary molarities of $(Li/Na)_2$ carbonate on LSCF-SDCc. Different binary molarities may influence the chemical behavior the composite cathode. In addition to that, issues regarding particle coarsening or microstructural changes at elevated temperature or pro-longed operation have become a concern as these greatly affect the long-term stability of the cathode. The phase and microstructural stability is another key aspect to ensure cell stability of the cell and maintaining the cell power density (Haider et al. 2011; Harris et al. 2013; Muhammed Ali 2020). To the best of our knowledge, no studies has been performed on the effects of $(Li/Na)_2$ carbonate molarities on the long-term microstructural and phase stability of LSCF-SDCc.

Given this consideration, this work aims to investigate the influence of various binary $(Li/Na)_2$ carbonate molarities on the long-term phase and microstructural stability of LSCF-SDC composite cathode. Three different molar ratios of $(Li/Na)_2$ carbonate (i.e. 67:33, 62:38, and 53:47 mol.%) were selected to prepare LSCF-SDCc cathode powders via high energy ball milling. The selection range of the carbonate molar ratios was based on previous studies that showed promising electrochemical characteristics (Patakangas et al. 2014). Next, the crystalline phase and microstructural changes were evaluated based on long-term stability of 1000 h at 400 and 600 °C, respectively.

MATERIALS AND METHODS

PREPARATIONS OF LSCF-SDCC COMPOSITE CATHODE POWDERS

Commercial powders consist of SDC, Li_2CO_3 , Na_2CO_3 (Sigma Aldrich, USA), and LSCF6428 (Kceracell, South Korea) in their size of 300-600, 800, and 400 nm, respectively, were utilised in this study. A two-step processes were used to prepare the LSCF-SDCc composite cathode powders. In the first step, samarium-doped ceria-carbonate (SDCc) electrolytes were produced by combining 20 wt. % $(Li/Na)_2$ carbonate in various carbonate molar ratios (i.e. 67:33, 62:38, and 53:47 mol.%), with 80 wt. % SDC using wet-ball milling process. This milling process was performed in a 250 mL zirconia jar for 24 h (Fritsch Pulverisette 6, Germany). Subsequently, the electrolyte slurry was oven-dried at 80 °C for 24 h and arranged for calcination process at 680 °C for 1 h.

In the second step, the obtained SDCc electrolytes and commercial LSCF6428 (300-600 nm) powders were mixed at a weight ratio of 50:50. High-energy ball milling, (HEBM) was employed to obtain homogeneous mixture of the composite cathode powders. Subsequently, the composite cathode mixtures were dried overnight and calcined at 750 °C for 2 h (Huang et al. 2010).

FABRICATION OF LSCF-SDCC COMPOSITE CATHODE PELLETS AND SYMMETRICAL CELLS

Two types of cells were fabricated: green cell LSCF-SDCc composite cathode pellets (0.8 mm thickness and 13 mm diameter); and SDCc||LSCF-SDCc||SDCc symmetrical cells (1 mm thickness and 13 mm diameter). The green cells were prepared to investigate the durability and stability of the composite cathode. On the other hand, the symmetrical cells were prepared for electrochemical performance testing. Both cells were fabricated using cold uniaxial press technique with an applied pressure of 47 MPa and a holding time of 1 min. Afterwards, the green cells were sintered for 90 min at 600 °C with a heating and cooling rate of 5 °C min⁻¹ in air. Henceforth, the sample with various (Li/Na)₂ carbonate molarities of 67:33, 62:38, and 53:47 mol.% were then designated as LSCF-SDCcM1, LSCF-SDCcM2, and LSCF-SDCcM3, respectively.

CHARACTERIZATION OF POWDERS AND SYMMETRICAL CELLS

The chemical and crystalline phases of the composite cathodes were examined using an X-ray diffractometer (XRD) (Bruker D8 Advance, Germany) using Cu K α as radiation source ($\lambda = 0.15406$ nm). A scanning range (2θ) of 20 to 80° and a step scan step of 0.02° were employed to collect the XRD patterns. Fourier transform infrared spectrometer was employed to obtain the infrared (IR) spectra of the composite cathode based on attenuated total reflectance method with a spectra range of 4000-550 cm⁻¹ (Spectrum 100, Perkin Elmer, USA).

The elemental distributions of the composite cathode were investigated using scanning electron microscope (Hitachi Table Top 3030, Japan) coupled with energy-dispersive spectroscopy (EDS). Field emission scanning electron microscopy (FESEM, Zeiss Supra 55VP, Germany) was used to observe the cross-sectional morphologies of the composite cathodes. A digital micrograph software (Smart Tiff) was used to measure the particle size of the composite cathode based on the FESEM micrograph. The particle size is also determined using Zeta-Sizer Nano (Zeta-Sizer ZS, UK) based on dynamic light scattering with absolute ethanol as dispersant. Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area of the composite cathode powders through

nitrogen physisorption at -196 °C and tested within the pressure range of 0.05-0.30 (ASAP 2020, Micromemetrics, USA). A horizontal dilatometer was used to examine the thermal expansion coefficient (TEC) of the composite cathode tested within 30-600 °C in air. Alumina was used as standard reference sample for dilatometry analysis (L75H-Linseis, Germany). The Archimedes method was used to examine the open porosity of the sintered composite cathode pellets via a density kit (Mettler Toledo, USA).

The durability test was carried out for the composite cathode pellets by using the tube furnace (Elite Thermal System Limited, Germany). The pellets were exposed to a heat at 400 until 600 °C for 1000 h (Mehran et al. 2016) under open circuit conditions. The ionic conductivity of the composite cathode was measured via electron blocking technique, whereby SDCc electrolyte was used as an electron blocking layer. The as-prepared SDCc||LSCF-SDCc||SDCc symmetrical cells prepared earlier were used for the conductivity measurements. Silver conducting paste were applied on both sides of the cells and heated at 150 °C for solvent evaporation prior to testing. The symmetrical cell was placed on a two-point platinum probe sample holder to obtain the conductivity of the composite cathode. The test was performed at 400 to 600 °C under static air condition using an Autolab PGSTAT302N equipped with a frequency response analyser (Autolab 302 FRA, Netherland). A frequency ranges of 100 kHz to 0.1 Hz and a low amplitude voltage of 10 mV was applied. The acquired impedance spectra were analysed using Nova software (Version 1.10.5). The area specific resistance (ASR) is calculated based on the $ASR = (R \times S)/2$, where R is the interfacial resistance and S is the surface area (1.33 cm²).

RESULTS AND DISCUSSION

CHEMICAL AND PHASE IDENTIFICATIONS

Figure 1 shows the XRD profile of LSCF-SDCc composite cathodes prepared on various (Li/Na)₂ carbonate molar ratios, before and after long-term durability for 1000 h at 400 and 600 °C. The standard pattern of cubic LSCF (JCPDS No. 01-089-1268) and SDC (JCPDS No. 01-075-0157) were observed, respectively. None of the (Li/Na)₂ carbonate peaks were detected in all XRD diffractograms which confirms their presence as an amorphous phase (Jaiswal et al. 2015). In addition to that, low intensity peaks of strontium carbonate (SrCO₃) (JCPDS No. 00-005-0418) can be observed in all diffractograms. As reported in our previous study, the formation of SrCO₃ (at $2\theta = 20$ to 45°) appeared after processing of composite cathode with HEBM process (Harris et al. 2013). This is normally caused by excessive power generated that might have triggered

the minor phase of SrCO_3 to form during milling process with commercial LSCF powders.

However, these observations are common and consistent with other researchers (Jarot et al. 2015; Jiang et al. 2011). Notably, the peak intensities of the SrCO_3 also remain low and gradually diminish at 600°C after prolonged from 0 to 1000 h, as illustrated in Figure 2.

Overall, no other formation of secondary phases can be observed. Thus, the current finding signify that the composite cathodes retain their phase stability after long-term durability for 1000 h, which is an essential characteristic to ensure good cathodic electrochemical performance.

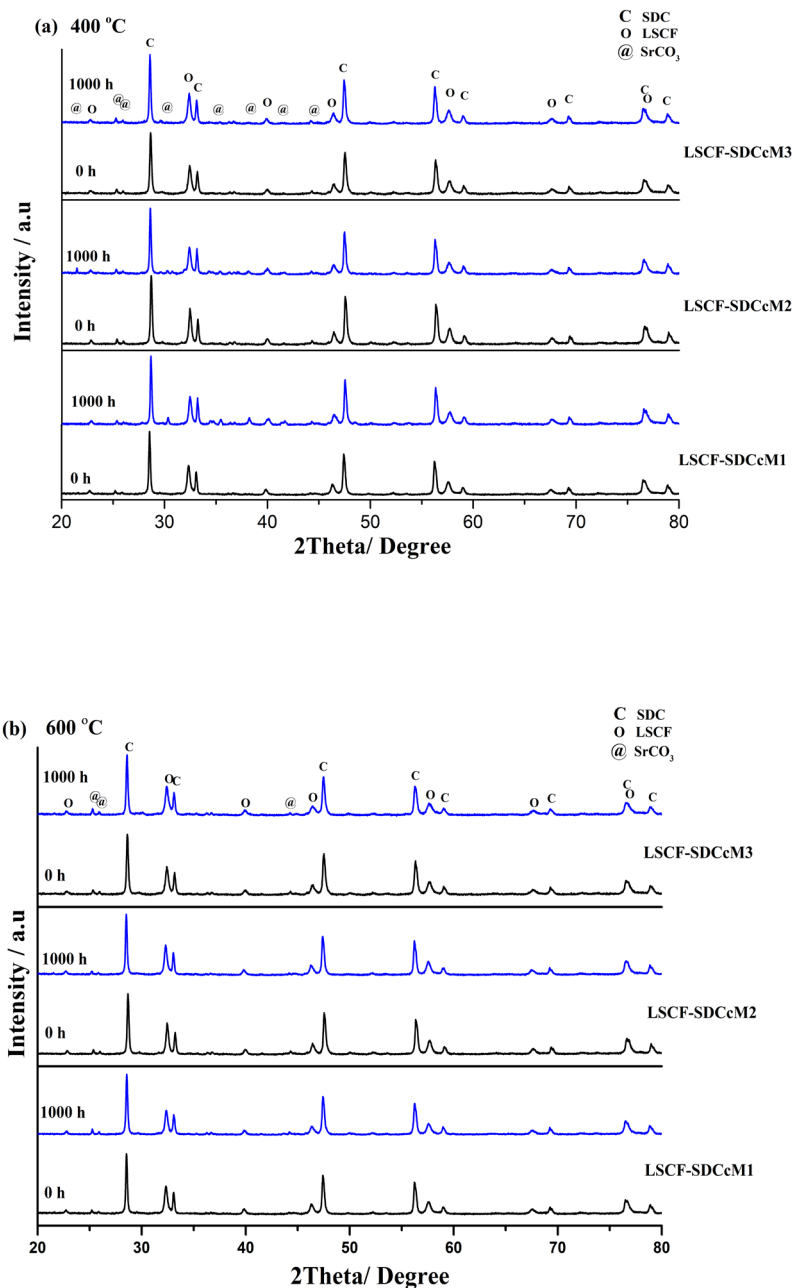


FIGURE 1. XRD profile of LSCF-SDCcM1, LSCF-SDCcM2, and LSCF-SDCcM3 composite cathodes prepared using various $(\text{Li}/\text{Na})_2$ carbonate molar molarities: before (0 h) and after long-term durability (1000 h) (a) 400°C , and (b) 600°C

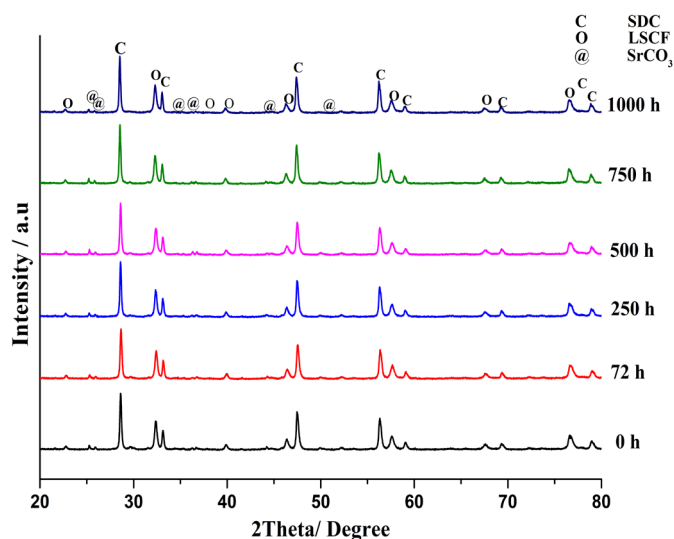


FIGURE 2. XRD profile of LSCF-SDCcM2 after prolonged at 600 °C

THERMAL EXPANSION COEFFICIENTS (TEC)

Thermal mismatch between SOFC components have been a major concern for operation, thermal cycles and even during fabrication. Therefore, tailoring the thermal expansion as close to the electrolyte can prevent cell delamination and microcracks that are essential to maintain and ensure power density stability (Jing et al. 2013). Table 1 shows the TEC of LSCF-SDC composite cathodes based on various $(\text{Li/Na})_2$ carbonate molarities obtained

within 30 to 600 °C. In this analysis, the TEC difference was evaluated based on the prepared SDCC electrolytes as reference to the composite cathodes. LSCF-SDCcM3 produced the lowest TEC mismatch of 1.37% with the SDCCM3 electrolyte as compared to LSCF-SDCCM1 and LSCF-SDCcM2 with TEC difference of 2.80 and 6.64%, respectively. Nonetheless, all samples yielded a permissible TEC difference of 10% for cathode components to avoid cell delamination and it is expected to provide good electrochemical performance (Choi et al. 2017).

TABLE 1. Average TEC and composite cathode LSCF-SDCc prepared at various $(\text{Li/Na})_2$ carbonate molarities

Sample	TEC (10^{-6} K^{-1}) (30 °C - 600 °C)	TEC difference (%)
SDCCM1	13.30	-
SDCCM2	12.86	-
SDCCM3	15.18	-
LSCF-SDCcM1	13.67	2.80
LSCF-SDCcM2	13.72	6.64
LSCF-SDCcM3	14.97	1.37

ELEMENTAL DISTRIBUTIONS AND IR CHARACTERIZATIONS

EDS mapping was conducted to verify the elemental distributions and homogeneity of the composite cathodes.

Morphology of LSCF-SDCcM2 in Figure 3 indicates the existence of La, Sr, Co, Fe, Sm, Ce, and Na. Moreover, all elements were well distributed within the mapped region which further verify the homogeneity of the composite

cathode powders. The homogeneity of the composite powder is important for enhancing the triple phase boundary (TPB) that contributes to ionic and electronic

paths for charge mitigation. Nevertheless, lithium (Li) cannot be observed using EDS due to low X-ray energy band (Khan et al. 2017).

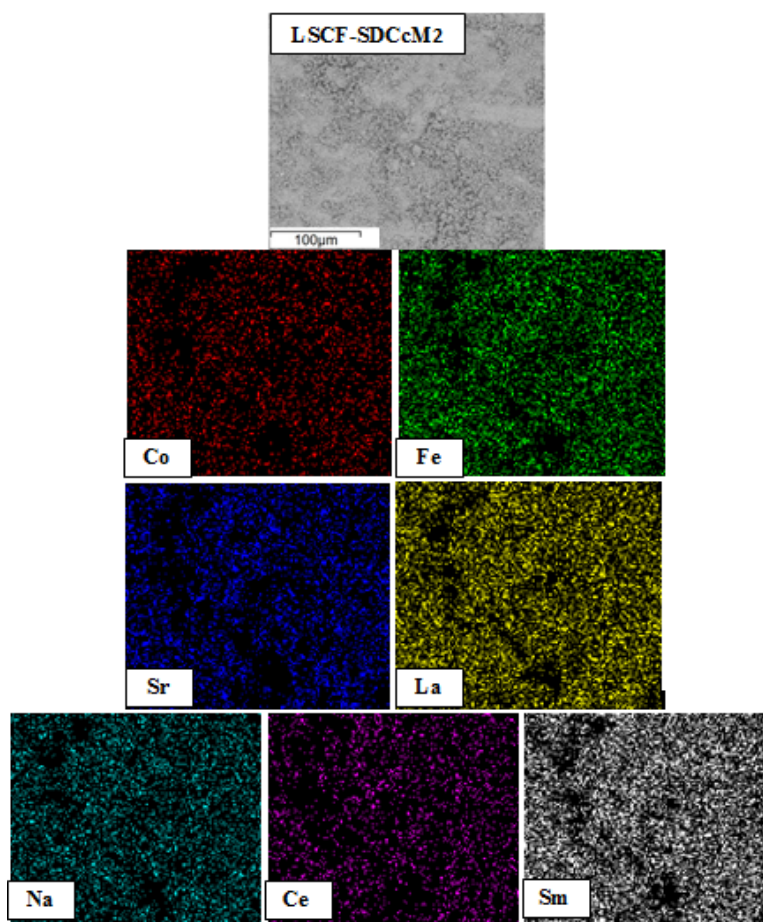


FIGURE 3. EDS mapping and elemental distributions for composite cathode LSCF-SDCcM2

The IR spectra of the composite cathodes is shown in Figure 4. Sharp bands were observed in all spectra at the region of 1436 and 860 cm^{-1} that corresponded as stretching and bending vibrations of the CO_3^{2-} bonds. In addition, small peaks located at 850 - 1600 and 2800 - 3000 cm^{-1} were mainly due to the Ce–O in stretching mode (Li et al. 2017; Liu et al. 2017). Besides that, weak bands located at the region 3400 - 3500 cm^{-1} were mainly attributed to bending of O–H bonds originated from the ambient moisture (Ma et al. 2010). As for quantitative comparison, the lowest intensity signals of the carbonate

peaks recorded for LSCF-SDCcM3. This is due to lower eutectic melting point of LSCF-SDCcM3 ($\sim 512\text{ }^\circ\text{C}$), as compared to LSCF-SDCcM1 ($588\text{ }^\circ\text{C}$) and LSCF-SDCcM2 ($563\text{ }^\circ\text{C}$) (Muhammed Ali et al. 2013). When the composite cathode powder exposed to the calcination temperature of $750\text{ }^\circ\text{C}$, the carbonate signal intensities decreased due to melting and degradation of carbonate. Nonetheless, the IR spectra of all composite cathode powders still exhibit the presence of carbonate that is essential for maximizing the O^{2-} transfer (Chen et al. 2014).

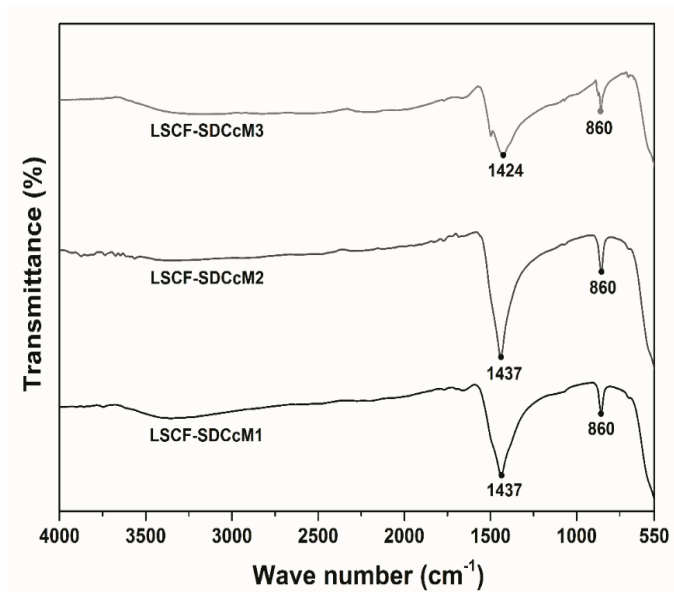


FIGURE 4. FTIR spectra for LSCF-SDCc composite cathode powders based on different carbonate molarity

MORPHOLOGIES OF COMPOSITE CATHODE POWDERS

Effects of various $(\text{Li}/\text{Na})_2$ carbonate molarity on the powder morphologies were further studied via FESEM (Figure 5). Figure 5 shows fine particle of about ~ 100 nm observed in all composite cathode powders, which was obtained from HEBM process. HEBM process is advantageous to produce fine and well distributed powders that saves milling time of up to 70% as compared to low speed milling (150-200 rpm) (Giuliano et al. 2017; Muhammed Ali et al. 2017). The particle size obtained from Zeta-Sizer and FESEM particle measurement are tabulated in Table 2. LSCF-SDCcM3 (86.01 nm) consist of slightly larger particle size followed by LSCF-SDCcM1 (85.45 nm) and LSCF-SDCcM2 (82.03 nm). This finding

is much related to the calcination process of the composite cathode. When calcination temperature (750°C) applied exceeds the eutectic melting temperature of the carbonate; the carbonate melts and covers the particle to form a core-shell. This presence of molten carbonate is necessary so that core-shell can be formed to protect the particle from energetic growth (Li et al. 2015; Muhammaed Ali et al. 2017). Therefore, LSCF-SDCcM3 which has low eutectic melting temperature ($\sim 512^\circ\text{C}$) as compared to LSCF-SDCcM1 and LSCF-SDCcM2 might have led to evaporation of carbonate that reduces the ability to protect the composite cathode powders from the energetic growth (Ma et al 2010; Patakangas et al. 2014).

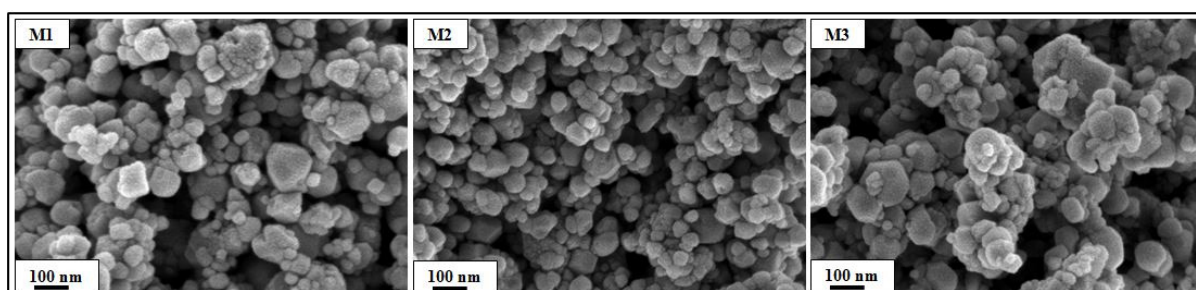


FIGURE 5. FESEM images of composite cathode LSCF-SDCc for: M1, M2 and M3 after HEBM and heat-treatment process

TABLE 2. Specific surface area, agglomerate size, particle size and porosity of composite cathode LSCF-SDCc

Samples	Specific surface area [m ² /g]	Agglomerate size (Dynamic light scattering) [nm]	Average particle size (Smart Tiff software) [nm]
LSCF-SDCcM1	1.56	276.53 (±7.32)	85.45 (±6.74)
LSCF-SDCcM2	9.02	297.48 (±5.16)	84.03 (±6.09)
LSCF-SDCcM3	3.60	270.58 (±6.40)	86.01 (±6.12)

The specific surface area (Table 2) of the composite cathode powders obtained from the BET analysis was 1.56, 9.02, and 3.06 m²g⁻¹ for LSCF-SDCcM1, LSCF-SDCcM2, and LSCF-SDCcM3, respectively. These values are within the range that is suitable for practical SOFC cathode application (~5-7 m²g⁻¹) (Rahman et al. 2012). Moreover, the obtained surface area is also in good agreement with other LSCF composite cathodes reported from previous studies. Rahman et al. (2013), Raza et al. (2017) and Rembelski et al. (2012) had reported the specific surface areas of 6.0, 4.7, and 3.7-7.40 m²g⁻¹ for LSCF-BZSY, LSCF-LSGM, and LSCF-SDCC composite cathode powders, respectively. The obtained specific surface area data is also consistent with the measured particle size from FESEM as discussed earlier, whereby larger particle will have lower surface area (Rahman et al. 2012). However, particle size obtained from zeta-sizer shows increment of about twice in size as compared to particle size measured from FESEM analysis. This could be due to the solidification of carbonate, whereby the carbonate covers the composite cathode powders after the calcination process. This commonly lead to loosely

particle agglomeration (Ristoui et al. 2012; Rondão et al. 2013). According to Baharuddin et al. (2013) in Shawuti and Gulgun (2014), the increase of particle size obtained from Zeta-Sizer could be also due to agglomeration in the suspension during analysis. In short, all composite cathode powders remain in below 100 nm with suitable surface area that potentially enhance the active sites for good electrochemical performance.

CROSS-SECTIONAL MORPHOLOGIES AND POROSITY OF COMPOSITE CATHODE PELLETS

Besides the powder properties, the microstructural characteristics of the pelletized composite cathode was investigated. The cross-sectional morphologies of the composite cathode pellets, before and after durability test at 600 °C for 1000 h, was observed using FESEM. Figure 6 shows minor increment of grain size after long-term durability test. However, the addition of (Li/Na)₂ carbonate leads to insignificant microstructural changes since no substantial abnormal growth can be observed after 1000 h.

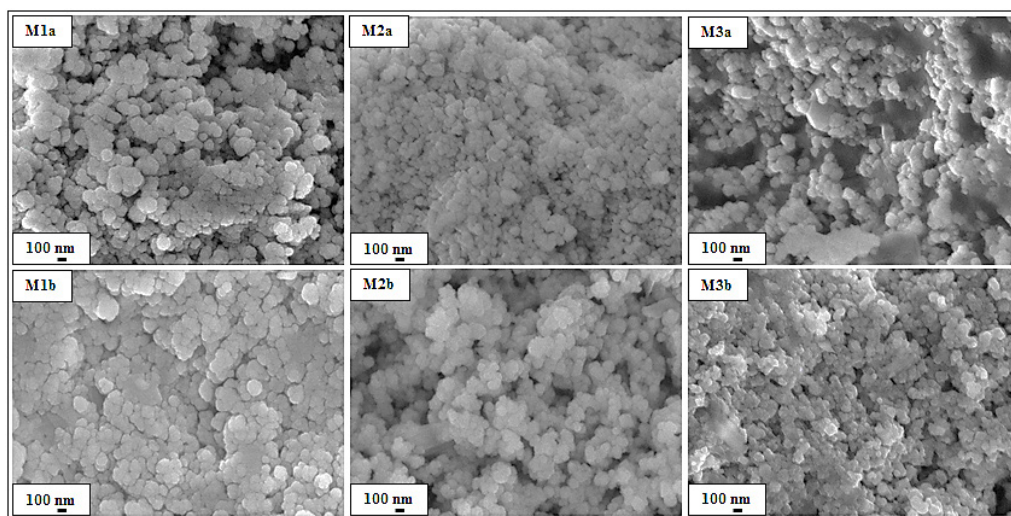


FIGURE 6. Cross-sectional FESEM image of composite cathode LSCF-SDCcM1, LSCF-SDCcM2 and LSCF-SDCcM3 pellets (a) before, and (b) after long-term durability

Archimedes principle was used to determine the porosity results for composite cathode of LSCF-SDCcM1, LSCF-SDCcM2, and LSCF-SDCcM3 before and after long-term durability test for 1000 h. As shown in Table 3 and Figure 6, a slight decline in porosity (1-3%) was observed for all samples after durability test. The porosity results decrease about 1 - 3% for all samples, which mainly attributed to the minor increment of particle size as observed in Figure 6. This finding suggests that the existence of $(\text{Li/Na})_2$ carbonate on LSCF-SDCc

demonstrated slight influence on the porosity level and microstructure after long-term durability test for 1000 h. Moreover, the melting $(\text{Li/Na})_2$ carbonate flows into the gaps of the pore, may indirectly decrease the porosity level of the composite cathode LSCF-SDCc (Fan et al. 2017). Nonetheless, the porosity level of the composite cathodes presented in this study are still within the adequate range (20-40%) to maintain good TPB for SOFC application (Rembelski et al. 2012).

TABLE 3. Porosity of composite cathode LSCF-SDCc before and after long-term durability for 1000 h

Samples	Porosity [%]	
	0 h	1000 h
LSCF-SDCcM1	27.41	24.21
LSCF-SDCcM2	25.78	23.01
LSCF-SDCcM3	28.83	27.18

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ANALYSIS

To further evaluate the effects of $(\text{Li/Na})_2$ carbonate on the LSCF-SDCc composite cathodes, electrochemical impedance spectroscopy was performed. Figure 7 shows the Nyquist plot for the symmetrical cells of SDCc|LSCF-SDCc|SDCc obtained at 400, 500 and 600 °C under open circuit condition. In a typical Nyquist plot, the high-frequency intercept of the impedance spectrum provides the ohmic resistance of the cell. Resistance associated at high-frequency is normally reflects the charge-transfer processes that include electron-transfer and ion-transfer processes at the interfaces of the current collector-cathode, and a at the cathode-electrolyte (Shen & Lu 2015).

The impedance spectra were fitted with the typical equivalent circuit shown in Figure 8. The circuit consist of $R_{\text{ohm}}(R1\text{-CPE1})(R2\text{-CPE2})(R3\text{-CPE3})$, where R_{ohm} corresponds to ohmic resistance, R corresponds to resistance and CPE as the constant phase element. The parallel element (R1-CPE1) signifies ionic conductivity. Meanwhile, (R2-CPE2) and (R3-CPE3) denote the charge transfer at TPB (grain boundary conduction) and oxygen gas adsorption-diffusion limiting processes, respectively (Khan et al. 2017). The R_{ohm} intercept with the real axis at high frequencies provides ohmic resistance (Shen & Lu 2015).

The fitting results of the impedance spectra are shown in Table 4. In this study, $(\text{Li/Na})_2$ carbonate molarities affects the resistance of the composite cathode. The total resistance of all cell reduces with the increase of temperature (400-600 °C) of up to one order magnitude. This phenomenon could be due to the molten state of carbonate that soften slightly above their transition temperature (eutectic melting points > 500 °C) which able to create more interfaces for enhanced ionic conduction as well as improving the charge transfer at TPB. Below the eutectic melting point, the ionic conduction are possibly blocked and retarded due to solidification of carbonates, hence creating large interfacial resistance and low conductivity. This finding is consistent with several authors (Tang et al. 2010; Zitouni et al. 2007).

There was a slight increment of area specific resistance (ASR) for LSCF-SDCcM2 at 500 °C which can be contributed from the smaller particle size that provided larger surface area for chemical reaction compared to the other cathode composition. LSCF-SDCcM2 yielded the smaller ASR of 201.3, 11.90 and 0.66 $\Omega\cdot\text{cm}^2$ at 400, 500 and 600 °C, respectively, as compared to other cells. This finding is also coherent with largest specific surface area and smallest particle size results as discussed earlier, that promote reaction sites for charge transfer and gas absorption which strongly influence on the resistance of LSCF-SDCcM2.

TABLE 4. Resistance and conductivity for composite cathodes from 400 to 600 °C

Temperatures	Samples	Area specific resistance, ASR [$\Omega \cdot \text{cm}^2$]	Conductivity, σ [$\times 10^{-2} \text{ S cm}^{-1}$]
400 °C	LSCF-SDCeM1	266.6	0.002
	LSCF-SDCeM2	201.3	0.003
	LSCF-SDCeM3	691.7	0.007
500 °C	LSCF-SDCeM1	9.90	0.050
	LSCF-SDCeM2	11.90	0.042
	LSCF-SDCeM3	13.88	0.036
600 °C	LSCF-SDCeM1	0.69	0.164
	LSCF-SDCeM2	0.66	0.753
	LSCF-SDCeM3	3.30	0.538

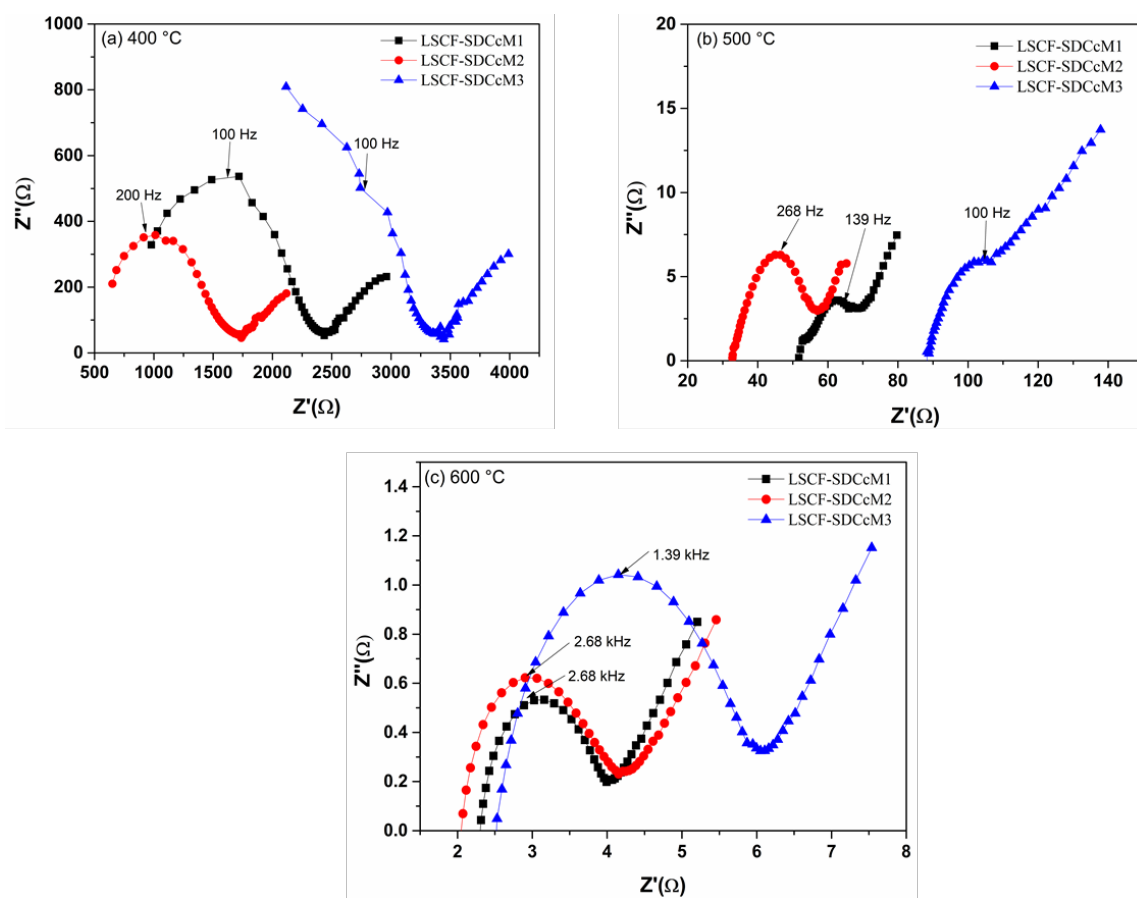


FIGURE 7. Impedance spectra plots of the SDCc|LSCF-SDCe|SDCc obtained at (a) 400, (b) 500, and (c) 600 °C

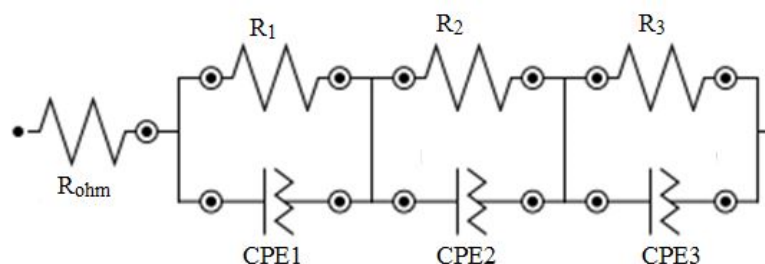


FIGURE 8. Equivalent circuits used for impedance spectra fitting

CONCLUSION

In this study, a homogeneous distribution of LSCF-SDCc phase based on various binary (Li/Na)₂ carbonate molar ratios were successfully prepared using HEBM. By careful structural and morphological studies of resultant composite cathodes using XRD, FESEM, and EDS mapping, the binary (Li/Na)₂ carbonate phases exhibit good compatibility of the composite cathode powder. No new compound or chemical reaction is found which signifies good structural stability between the (Li/Na)₂ carbonate phase structure and LSCF-SDCc phases after durability test for 1000 h. Uniform distribution was observed over the composite cathode of about 100 nm was formed. In addition to that, slight microstructural changes were observed and a slight decrease in porosity level (1 - 3%) was found after durability test. Furthermore, the current finding also proved that the binary (Li/Na)₂ carbonate molarity greatly influenced the resistance of the composite cathode LSCF-SDCc cells. Among them, LSCF-SDCcM2 with 62 mol% Li₂CO₃:38 mol% Na₂CO₃ shows the lowest area specific resistance (0.66 Ωcm²) and the smallest particle even after long-term durability at 600 °C for 1,000 h in air atmosphere. The long-term electrochemical performance is planned for future study.

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