Effect of sintering temperature on surface morphology and electrical properties of samarium-doped ceria carbonate for solid oxide fuel cells

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Abstract

The effects of sintering temperature on the surface morphology, roughness, and electrical properties of samarium-doped ceria (SDC)–carbonate (SDCC) composite electrolyte were examined. SDCC composite pellets were fabricated and sintered at various temperatures ranging from 500 °C to 650 °C. Brunauer–Emmett–Teller technique and atomic force microscopy were used to investigate the surface area and surface roughness of the composite materials, respectively. Conductivity measurements using impedance spectroscopy were conducted from 350 °C to 550 °C. The specific surface area of the pure SDC powder decreased from 8.85 m²/g to 4.24 m²/g after the carbonate phase was incorporated into the SDC phase with increasing particle size. The composite pellet sintering temperature affected the continuity between the two phases [SDC and (Li/Na) carbonate], roughness, mean particle size, and conductivity of the composite electrolyte. A fully dense SDCC composite electrolyte pellet sintered at 550 °C exhibited a maximum ionic conductivity of 0.077 S/cm at 550 °C. In addition, 550 °C was the minimum sintering temperature to achieve good wetting between the two phases, moderate particle size, low surface roughness, and high ionic conductivity.

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1. Introduction

Solid oxide fuel cells (SOFC) are among the most efficient fuel cells that operate at high temperatures to convert chemical energy into electrical energy [1–4]. Zirconia-based electrolytes, such as yttria-stabilized zirconia (YSZ), are commonly used because of their high ionic conductivity (> 10⁻¹ S/cm), high efficiency, and excellent chemical and thermal stabilities in both oxidizing and reducing environments. YSZ-based SOFCs are usually operated at temperatures reaching 800 °C to 1000 °C [5,6]. Han et al. [7] reported the maximum power density of 0.95 W/cm² at 800 °C for YSZ electrolyte-based anode-supported SOFCs using hydrogen as fuel and air as oxidant. Reducing the operating temperature can increase the lifetime and can expand the choices for the constituent materials [8]. In recent studies, the operating temperature was reduced by the development of new electrolyte materials [9,10]. Ceria-based electrolyte materials, such as samarium-doped ceria (SDC) or gadolinium-doped ceria, offer the best ionic conductivity at operating temperatures between 400 °C and 800 °C [11,12]. However, ceria-doped electrolytes tend to easily reduce at low oxygen partial pressure, thereby exhibiting high electronic conductivity in an anodic background [13]. This electronic conduction results in a great loss in cell performance and exhibits poor mechanical strength.

Increased ionic conductivity and electronic conduction suppression of ceria-doped electrolytes can be achieved by introducing a small amount of alkaline salts [14–16]. Ceria–carbonate...
composite electrolytes exhibit higher ionic conductivity (10−2 S/cm to 1.0 S/cm) and power density (400 mW/cm² to 1700 mW/cm²) in the intermediate temperature range than pure SDC [14]. The ionic conductivity of ceria-based electrolytes can be influenced by various interrelated factors, such as grain boundary, grain size, particle shape, composition, and processing. The composition and processing conditions can significantly alter the electrolyte powder properties and overall performance of the cell. The effects of these factors on ceria-based electrolytes have been discussed in other studies [16–20].

Xia et al. [21] studied the influence of different surface properties of SDC powder prepared using the sol–gel (SG), glycine–nitrile (GN) and co-precipitation method on the performance of SDC–carbonate (SDCC) composite electrolyte. They found that the surface properties of SDC (powder structure, surface area and interface between SDC and carbonate phase) and electrolyte thickness significantly influence the performance of fuel cells. They also recognized that ionic transport and thermal behavior of SDCC composite electrolyte strongly depend on the surface property of SDC. Powders with rod-like SDC particles prepared by oxalate co-precipitation show the best performance because of the formation of the consecutive interface and dual-phase (SDC and carbonate phase) in ionic conduction. In addition, the performance of SDCC composites can be improved by increasing the interfacial area. SDC powders prepared by the GN and SG methods shows slightly poor performance because of poor interfacial conduction area formation. Powders prepared using the GN and SG methods exhibit foam-like (porous structure) and agglomerated (core-like structure) SDC, respectively, which may destroy the interfacial conduction path and limit the carbonate phase continuity.

Bodèn et al. [22] achieved high ionic conductivity and low activation energy for the composite electrolyte with 80% SDC and 20% (Li/Na) carbonate. They found that conductivity strongly depends on the carbonate content. Two phases of SDCC composite electrolyte powders were formed in a mixture of 10% (Li/Na) carbonate and 20% (Li/Na) carbonate. Meanwhile, large (Li/Na) carbonate crystals without a continuous phase with SDC particles were formed in a mixture with 50% (Li/Na) carbonate. They also recognized that different gas environments do not strongly influence the conductivity of SDCC composites. According to Zhu et al. [20], conductivity can be enhanced several times compared with pure SDC when the carbonate content is less than 30%.

The processing condition is another important factor that influences the electrical conductivity of electrolytes. This factor includes the different sintering techniques to prepare ceramic pellets with controlled microstructures, such as grain size, density, and purity. In our recent work [23], we investigated the electrical conductivities of pellets sintered at different temperatures based on current–voltage characteristics in SDCC composite electrolyte. We have identified that the pellet sintered at 550 °C has the best microstructure with less porosity, better open circuit voltage (OCV) and higher power density than pellets sintered at higher temperatures. This phenomenon is noticeably different with those reported by Xia et al. [24], who observed that the samples sintered at 675 °C for 2 h produces a superior interfacial microstructure, 98.9% density, and better ionic conductivity than pellets sintered at 600 °C, 625 °C, 650 °C and 700 °C.

The aforementioned examples indicate that the factors such as composition, processing condition and micro-structure influence the performance of SDCC composite electrolytes. Surface roughness and physical treatment also influence the electrolyte properties, particularly the carbonate phase melting of (Li/Na) carbonate to form a continuous phase with SDC particles. Although numerous studies have reported on the performance of SDCC composite electrolyte, reports on the effect of sintering temperature on surface roughness and the consequent electrical properties are limited. Therefore, in this study we focused on the effects of sintering temperature on the surface roughness, and electrochemical properties of SDCC composite electrolytes. The surface roughness and surface morphology of SDCC composite electrolyte pellets sintered at various temperatures were examined using atomic force microscopy (AFM). The grain size growth of the pellets sintered at various temperatures ranging from 500 °C to 650 °C was observed by field-emission scanning electron microscopy (FESEM). Electrochemical impedance spectroscopy (EIS) was also applied to investigate the ionic conductivity of the SDCC composite electrolytes from 350 °C to 550 °C.

2. Experimental procedure

SDC with Ce0.8Sm0.2O1.9 composition was prepared using citrate SG-based methods [25]. SDCC composite electrolyte powder was prepared by the solid-state reaction method [23]. The pure SDC and SDCC composite electrolyte powders were obtained after calcining at 850 °C for 5 h and at 680 °C for 1 h, respectively. A detailed description of the preparation procedure of the SDC and SDCC composite electrolyte powders is available in a previous publication [23]. X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (Shimadzu XRD-6000, Germany) with CuKα (λ = 1.5418 Å) radiation and 2θ ranging from 20° to 80° to identify the crystalline phase of the pure SDC and SDCC composite powders. The specific surface areas of the pure SDC and SDCC calcined powders were measured using a surface area analyzer (Micrometrics, ASAP 2010, USA) and the Brunauer–Emmett–Teller technique. Pore size and volume were calculated using the Barrett–Joyner–Halenda cumulative adsorption and desorption methods.

The SDCC composite electrolyte powders were cold-pressed at 80 MPa into 25 mm-wide and 1 mm-thick cylindrical pellets using a uniaxial die-press. The as-prepared green pellets were sintered at 500, 550, 600, and 650 °C for 5 h in air and then designated as 500SDCC, 550SDCC, 600SDCC, and 650SDCC, respectively. FESEM (Zeiss Supra-55VP) was used to examine the microstructure, particle size, shape, and morphology of the SDCC composite pellets. AFM was used to investigate the roughness and surface morphology of the sintered pellets before electrochemical impedance measurement. AFM raw data were processed and analyzed using NOVA (Version: 3.5.0.2069) software.

The conductivities of the SDCC composite electrolytes were measured at temperatures from 350 °C to 550 °C using impedance
spectroscopy. Silver paste was applied to both sides of the sintered samples and heated at 150 °C for 15 min. The effective working area of the pellet was 1.3 cm². The measurements were conducted at 50 °C intervals in static air. The sample was stabilized at a given temperature for 2 h before the measurement was performed. The test was performed in potentiostatic mode using an Autolab PGSTAT302N coupled with a frequency response analyzer (Autolab 302, Eco Chemie, Netherlands) over a frequency range of 10⁶–0.1 Hz under a low-amplitude sinusoidal voltage of 10 mV. The data acquired from the impedance testing were analyzed using NOVA-software (Version 1.9). To measure conductivity, the AC-impedance diagrams were plotted in $Z' \text{ (real)}$ versus $Z'' \text{ (imaginary)}$ for the composite pellets sintered at different temperatures.

3. Results and discussions

3.1. Crystal phase by XRD

The crystal phase of the pure SDC and SDCC composites was analyzed by XRD after calcining at 850 °C and 680 °C, respectively. The XRD patterns of the SDCC composite powders exhibited a cubic fluorite structure with a space group of Fm3m (JCPDS File no. 34-0394), which represented the SDC phase (Fig. 1). Moreover, no extra peaks were observed when the XRD phase of the SDCC composite was compared with that of pure SDC powder. The XRD pattern showed that the peak positions of the SDCC composite were unchanged compared with that of pure SDC, and only the intensity of each peak increased after incorporating the composite effect. With the composite effect caused by adding (Li/Na) carbonate to the pure SDC and further calcination at 680 °C, the peak intensity of SDCC composite increased. Moreover, increase in peak intensity represented a better structural and crystallization formation. These results were in accordance with the increase in crystallite sizes of the SDCC composite.

The crystallite sizes of the calcined SDCC composite electrolyte and pure SDC electrolyte powders were determined according to the standard Scherrer’s equation given by $D = \frac{0.9\lambda}{\beta \cos \theta}$, where $D$ is the average size of particles, $\lambda$ is the wavelength of X-ray radiation (Cu Kα radiation = 0.15406 nm), $\beta$ is the full width at half-maximum of the diffracted peak, and $\theta$ is the angle of diffraction (Bragg angle). The crystallite sizes of the pure SDC and SDCC composite electrolyte powders calcined at 850 °C and 680 °C were calculated as 61 and 63 nm, respectively. The crystallite sizes of the SDCC composite slightly increased, thereby indicating that crystallization of SDC occurred after the addition of the (Li/Na) carbonate and calcination at 680 °C for 1 h. However, SDC electrolyte failed to show any structural change because the cubic, fluorite-like SDC and (Li/Na) carbonate existed as two distinct phases with no phase change. When the peak intensity and crystallite sizes of SDCC composite increased, no significant change in the XRD pattern and no new diffraction peaks from the carbonate phase were observed. These results demonstrated that no chemical reaction occurred or no new compound was formed during composite electrolyte preparation. Therefore, the mixture of (Li/Na) carbonate and SDC particles was not incorporated into the SDC lattice and mainly surrounded the SDC particles in amorphous form, which is in agreement with results of previous reports [22,25].

3.2. Specific surface area by gas adsorption using the BET technique

The pure SDC electrolyte powder had a specific surface area of 8.85 m²/g. The surface area of the SDC powders obtained in the

![Fig. 1. XRD pattern of the (a) pure SDC electrolyte and (b) SDCC composite electrolyte powder.](image-url)
The present study was higher than that of commercially available SDC powders [26] and previously reported powders [21,27,28]. A significant difference was observed in the specific surface area of the pure SDC powders after introducing (Li/Na) carbonate into the SDC matrix because of the increase in composite powder particle size. The SDCC composite electrolyte powder had a specific surface area of 4.24 m²/g. As expected, the specific surface area decreased as the particle size increased for the SDCC composite electrolyte because of the presence of macro-sized carbonates. The mean particle sizes of the pure SDC and SDCC composite powders were 50 and 81 nm, respectively [23]. The surface area decreased and particle size increased in the prepared SDCC composite powder after the incorporation of (Li/Na) carbonate. This difference may be attributed to the formation of loose agglomerated particles caused by the uniform distribution of (Li/Na) carbonate around the SDC particles during milling and calcination. However, this result does not affect electrolyte performance because macro-sized (Li/Na) carbonate particles melt at working temperatures (> 500 °C) and solidify below the transition temperature of (Li/Na) carbonate salt [23]. In addition, (Li/Na) carbonate acts as the gas diffusion layer to prevent gas crossover and facilitates high density at low sintering temperatures. This phenomenon results in the formation of a less porous electrolyte pellet with a low sintering temperature (550 °C) [23]. The SDCC composite surface area found in this study was higher than that in a previous report [21].

3.3. Surface morphology by FESEM

The cross-sectional field emission scanning electron microscopy images in Fig. 2 show the effect of sintering temperature on the melting characteristics and grain growth of SDCC composite electrolyte pellet. The melting of the (Li/Na) carbonate phase began when the sintering temperature was increased beyond the transition temperature of the carbonates (503 °C) [23]. When the sintering temperature was less than the melting point of the (Li/Na) carbonate, 500SDCC pellet showed inadequate melting of the (Li/Na) carbonate phase and a porous structure (Fig. 2a). By contrast, when sintered at higher than the melting point of the (Li/Na) carbonate (> 500 °C), the 550SDCC pellet showed a continuous interface between the SDC and (Li/Na) carbonate phases with no clear pores, and dispersal was uniform on the SDC grains (Fig. 2b). Increasing the sintering temperature to 600 °C and 650 °C showed that the two phases of SDC and (Li/Na) carbonate were not continuous. The two interfaces were clearly distinguished with the formation of large (Li/Na) carbonate particles melt at working temperatures (> 500 °C) and solidify below the transition temperature of (Li/Na) carbonate salt [23]. In addition, (Li/Na) carbonate acts as the gas diffusion layer to prevent gas crossover and facilitates high density at low sintering temperatures. This phenomenon results in the formation of a less porous electrolyte pellet with a low sintering temperature (550 °C) [23]. The SDCC composite surface area found in this study was higher than that in a previous report [21].

![Cross-sectional images of the SDCC electrolyte composite pellets sintered at different temperatures.](image-url)
The increase in sintering temperature not only acts on the (Li/Na) carbonate phase melting behavior but also increases the grain size of the SDCC composite electrolyte pellets. The mean grain size of the SDCC composite electrolyte pellets increased from 87 nm to 145 nm as the sintering temperature increased from 500 °C to 650 °C. The 550SDCC pellet showed a uniform distribution of (Li/Na) carbonate phase by surrounding the SDC particles with moderate particle sizes of approximately 120 nm (Fig. 2b).

3.4. Surface roughness by AFM

AFM was used to study the surface morphology and surface roughness of the SDCC composite electrolyte pellets. The three-dimensional (3-D) AFM images of the SDCC composite electrolyte pellets sintered at different temperatures ranging from 500 °C to 650 °C before EIS measurement are shown in Fig. 3. The melting of the (Li/Na) carbonate phase from the SDC phase was evident in the 3-D AFM images (Fig. 3a–d). The bright and dark colors represent the SDC and the (Li/Na) carbonate phase, respectively. When the sintering temperature increased from 500 °C to 550 °C, the surface roughness decreased from 21.20 nm to 13.7 nm. Thus, the surface became smoother because of the homogeneous melting distribution of (Li/Na) carbonate phase covering the SDC particles. However, the surface roughness increased drastically from 13.74 nm to 32.3 nm as the sintering temperature of the pellets reached 650 °C. This phenomenon may have been caused by the slight increase in particle size and the discontinuity of the (Li/Na) carbonate phase from the SDC phase at sintering temperatures > 550 °C, as evidenced by FESEM cross-sectional image. Therefore, the sintering temperature should be optimized to obtain moderate surface roughness and less porous structure for the SDCC composite electrolyte pellet.

3.5. EIS analysis

Conductivity of SDCC composite electrolytes was measured at 350–550 °C in static air. The impedance spectra of SDCC composite electrolytes sintered at different temperatures (500–650 °C) for 5 h were obtained at 450–550 °C (Fig. 4). The Nyquist plots typically show two arcs in the complex impedance plane. These arcs are usually related to the grain interior and grain boundary resistance at high frequency and electrode response at low frequency. The resistance of the high-frequency semicircle was used to calculate the total ionic
Conductivity of the sintered pellets [30]. The following equivalent circuits were used to investigate the electrical behavior over the temperature range: \( R(RQ)(RQ)(RQ) \) at 350–450 °C, and \( R(RQ)(RQ) \) at 500–550 °C, where \( R \) is the resistance (grain interior, grain boundary, and polarization of electrode) and \( Q \) is the constant phase element (CPE). The CPE was introduced to fix the depression below the baseline of semicircles, which is normal in ionic conductors [31].

The impedance spectra exhibit relatively depressed aspect of both high frequency arcs caused by the coexistence of several processes with different relaxation times. This distribution of relaxation processes may have resulted from the presence of two different phase materials involved in charge transport or different bonding mechanisms, as expected for the ceria–carbonate-based composite electrolyte. The sintered pellets showed combined or mixed performance from grain boundaries, which may have been caused by the presence of amorphous and continuous carbonate phase after melting and homogeneous distribution of two interfaces [SDC and (Li/Na) carbonate phases]. In addition, the arcs of sintered pellets became smaller with the increase in operating temperatures. At > 500 °C operating temperature, the interface between the SDC and (Li/Na) carbonate became continuous, and the molten (Li/Na) carbonate phase wetting covered the SDC substrate pores, which exhibited smallest arc for all the sintered pellets. The molten (Li/Na) carbonate filled the pores, thereby producing a gas-tight electrolyte. Below 500 °C, the arc became larger, probably as a result of the poor melting behavior of the (Li/Na) carbonate phase (503 °C). The ionic transport along the interface between the SDC and (Li/Na) carbonate phases was resisted because of the presence of the porous structure and absence of continuous molten carbonate network. Huang et al. [7], Xia et al. [24], and Tongxiang et al. [32] reported a similar conductivity behavior for SDCC composite electrolyte.

The plots of the typical Nyquist impedance spectra of 500SDCC, 550SDCC, 600SDCC, and 650SDCC at operating temperatures of 350, 500, and 550 °C are shown in Fig. 5. The arcs of SDCC composite electrolyte became smaller with the decrease in sintering temperatures. The smallest arcs of SDCC composite were obtained at sintering temperatures of 500 and 550 °C. The arcs became larger at > 550 °C sintering temperature. That is, SDCC composite sintered close to the melting point of (Li/Na) carbonate phase exhibited the lowest total resistance. In particular, 550SDCC showed the smallest arcs, operated at 550 °C, whereas 650SDCC shows the largest arcs, and thus, highest total resistance at all operating temperatures (Fig. 5). These impedance spectra are related to the interface between the two phases, homogeneous wetting of (Li/Na) carbonate phase and lowest roughness of 550SDCC.
Based on the FESEM image in Fig. 2b, 550SDCC is the best among the pellets sintered at different temperatures. This composite pellet exhibits good interfacial microstructure, uniform wetting of carbonate phase, moderate particle size, and minimum roughness. Thus, the pellets sintered close to the melting point of the carbonate phase enable the fastest transfer rate of ions along the interface between both phases, resulting in low total resistance. Moreover, the capacitance of the electrolyte is directly related to the surface roughness. Talebi et al. [31] proved that surface roughness, particle size, and particle density affect the shape of impedance curve. In addition, Li et al. [33] found that triple phase boundary length, large surface area, particle size, and uniform pore size strongly influence SOFC performance.

The performance at low operating temperature was evaluated to highlight the effects of sintering temperature on carbonate phase and particle size. The EIS plots for the 500SDCC, 550SDCC, 600SDCC, and 650SDCC composite electrolyte pellets measured at 350 °C operating temperature are shown in Fig. 5a. A similar impedance spectrum was also observed by Lapa et al. [34] at 350 °C operating temperature. The absence of grain boundary arc at 350 °C could be attributed to the influence of the carbonate phase. When operated at temperatures below the melting point of (Li/Na) carbonate phase (503 °C), the ionic transport along the interface between the SDC and (Li/Na) carbonate phases was resisted because of the presence of porous structure and absence of continuous molten carbonate network. The impedance of grain boundaries was evident across the SDC phase, where the ionic transport occurred [34]. Furthermore, when operated at temperatures below the melting point of (Li/Na) carbonate phase, the grain interior and grain boundary attribute high resistance. This phenomenon was due to the change in porosity because the grain interior and grain boundary conductivities largely depend on the porosity, microstructure, and roughness of the pellet [27]. The impedance spectra of the 500SDCC pellet were higher than those of the other sintered pellets (Fig. 5a). This result could be attributed to the segregation of the SDC and carbonate phases. Several studies have also reported the same difference in impedance curves with changing microstructure [27,29,31,35]. Therefore, these SDCC composite electrolyte materials should be sintered and operated beyond the melting point of (Li/Na) carbonate phase to achieve high ionic conductivity. The impedance curve significantly decreased with the decrease in sintering temperature of the composite pellets. The total resistance significantly changed as the sintering temperature decreased from 650 °C to 500 °C (Fig. 5).

The total ionic conductivity (σ) of all samples sintered at different temperatures was calculated as $\sigma = (1/R_{t.e}) \times (T/WA)$, where $T$
is the sample thickness (cm), \( R_{\text{el}} \) is the electrolyte resistance of the sample (\( \Omega \)), and \( W_A \) is the working area of the sample (cm\(^2\)). The electrical conductivity of the SDCC composite electrolyte pellets sintered at different temperatures was expressed in the form of an Arrhenius relationship given by \( \sigma T = A \exp(-E_a/kT) \), where \( E_a \) is the activation energy (J/mol), which normally includes energy terms for the formation and migration of oxygen vacancies, \( k \) is the Boltzmann constant \((1.3806503 \times 10^{-23} \text{ J/K})\), \( T \) is the temperature in Kelvin, \( A(\sigma_0) \) is the pre-exponential factor being a constant in a certain temperature range, and \( \sigma \) is the conductivity. The total ionic conductivity was plotted for \( \ln(\sigma T) \) as a function of reciprocal of temperature \((1000/kT)\). The pre-sintering temperature of \( 500^\circ \text{C} \) for all sintered samples, which corresponded to the melting point of (Li/Na) carbonate phase. This phenomenon could be characterized as superionic phase transition in the interfaces between the SDC and (Li/Na) carbonate phases \([36]\). With the increase in sintering temperature from \( 500^\circ \text{C} \) to \( 650^\circ \text{C} \), the total ionic conductivity decreased below \( 500^\circ \text{C} \) operating temperature and then rapidly increased with the increase in operating temperature (e.g., at \( 550^\circ \text{C} \)). This phenomenon could be explained by the melting characteristics of the (Li/Na) carbonate phase. When the sintering temperature became close to the (Li/Na) carbonate melting temperature \((503^\circ \text{C})\), the interface between the SDC and (Li/Na) carbonate became continuous and the molten (Li/Na) carbonate phase wetting covered the SDC substrate pores, which increased the ionic conductivity. Thus, the desirable superionic phase transition for ion conduction is closely related to the interface formation between SDC and (Li/Na) carbonate melting. The SDCC composite electrolyte pellets sintered at \( 550^\circ \text{C} \) show the highest total ionic conductivity (Fig. 6). The conductivities of \( 550^\circ \text{SDCC} \) were significantly higher than those of the samples sintered at relatively high temperatures. The total ionic conductivities of \( 550^\circ \text{SDCC} \), \( 600^\circ \text{SDCC} \), and \( 650^\circ \text{SDCC} \) were \( 0.077, 0.025, \) and \( 0.014 \text{ S/cm} \), respectively, at \( 550^\circ \text{C} \). The \( 550^\circ \text{SDCC} \) pellets showed better performance at all operating temperatures compared with the other samples. The relatively high performance of \( 550^\circ \text{SDCC} \) electrolyte was due to the closer connectivity of two-phase particles, which led to rapid ion transfer rate, resulting in high ionic conductivities (Fig. 6). Therefore, identifying the required sintering temperature is necessary to achieve optimal interfacial microstructure to provide the most feasible superionic phase transition for high ionic conductivity. The impedance results are consistent with the performance analysis, in which the composite electrolyte \( 550^\circ \text{SDCC} \) with the highest ionic conductivity generated the highest OCV of 1.14 V \([23]\).

The \( 550^\circ \text{SDCC} \) pellet achieved maximum conductivity of \( 0.077 \text{ S/cm} \) at \( 550^\circ \text{C} \), which was better than the results obtained by Gao et al. \([37]\), Ma et al. \([38]\), Gao et al. \([39]\), and Zhao et al. \([40]\). The measured ionic conductivities of the SDCC composite pellets were higher than that of pure SDC \([11]\). Compared with the total ionic conductivity of SDCC composite electrolyte sintered at \( 675^\circ \text{C} \) for \( 2 \text{h} \), \( 550^\circ \text{SDCC} \) showed a slightly lower conductivity. This slight difference in ionic conductivity and sintering ability of similar materials is possibly due to the differences in compositional homogeneity and microstructure of the products. Given that the corresponding powders were produced via modified sol–gel method, the microstructure and composition of the SDCC composite powders could exhibit different melting characteristics of the molten carbonate, and thus, requiring higher sintering temperature \((675^\circ \text{C})\). In this work, the total conductivity for \( 550^\circ \text{SDCC} \) sintered at \( 550^\circ \text{C} \) was close to those sintered at \( 675^\circ \text{C} \), suggesting that the powder produced via citric acid assisted sol–gel method had different microstructure and compositional homogeneity as well as very high sinterability. The \( 650^\circ \text{SDCC} \) pellet showed the lowest ionic conductivity \( (0.004 \text{ S/cm}) \) at \( 500^\circ \text{C} \). This result could be attributed to the porosity from poor wetting between the SDC and carbonate phases. However, the conductivity increased up to \( 0.014 \text{ S/cm} \) when the operating temperature reached \( 550^\circ \text{C} \). This result could be attributed to the melting of (Li/Na) carbonate, which covered the pores of the SDC phase, forming a gas-tight layer. At \( > 500^\circ \text{C} \) operating temperature, the total ionic conductivity increased for all of the sintered samples. This high conductivity was achieved when the operating temperature was above the melting temperature of (Li/Na) carbonate. This finding confirms that ionic conductivity is considerably influenced by sintering temperatures with respect to surface morphology, interfacial microstructure, distribution of (Li/Na) carbonate in SDC, and particle size of the composite electrolyte pellets. Therefore, \( 550^\circ \text{C} \) is the minimum sintering temperature required to achieve high ionic conductivity, moderate particle size, and low surface roughness.
4. Conclusion

SDCC composite electrolyte pellets containing 20 wt% carbonates were developed by sintering at various temperatures (500–650 °C). Surface roughness, continuity between two phases, and ionic conductivity of the composite electrolytes were remarkably affected by the sintering temperature. At temperatures above the transition temperature, the composite electrolyte pellet exhibited high ionic conductivity. The intermediate sintering temperature (550 °C) close to the binary (Li/Na) carbonate phase melting offered the best surface morphology, moderate particle size, and maximum ionic conductivity. Furthermore, 550 °C was the minimum sintering temperature to achieve moderate particle size and low surface roughness. In addition, continuity between the two phases was uniformly formed at 550 °C. The SDCC composite electrolyte pellet sintered at 550 °C exhibited the highest ionic conductivity. These studies confirm that the sintering temperature not only have a great impact on the microstructure but also interfacial microstructure interactions of the two-phase SDCC composite electrolyte.

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References

[1] S.C. Singhal, K. Kendall, High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, first ed., Elsevier Advanced Technology, Oxford, 2003.
[2] M.R. Somalu, V. Yuftit, D. Cumming, E. Lorente, N.P. Brandon, Fabrication and characterization of Ni/SnSZ cermet anodes for IT-SOFCs, Int. J. Hydrogen Energy 36 (2011) 5557–5566.
[3] A.R. Haminah, A. Muchtar, N. Muhamad. H. Abdullah, Structure and thermal properties of La0.68Sr0.32O3–CO3/F0.65O1.15–SDC carbonate composite cathodes for intermediate- to low-temperature solid oxide fuel cell, Ceram. Int. 38 (2012) 1571–1576.
[4] D. Panuh, A. Muchtar, N. Muhamad, E.H. Majlan, W.R.W. Daud, Fabrication of thin Ag–YSZ composite cathode film for intermediate- temperature solid oxide fuel cells, Compos. Part B: Eng. 58 (2014) 193–198.
[5] S. Hui, J. Roller, S. Yick, X. Zhang, C. Deces-Petit, Y. Xie, R. Maric, D. Ghosh, A brief review of the ionic conductivity enhancement for selected oxide electrolytes, J. Power Sources 152 (2007) 493–502.
[6] J. Huang, F. Xia, C. Wang, Z. Mao, Development of solid oxide fuel cell materials for intermediate-to-low temperature operation, Int. J. Hydrogen Energy 37 (2012) 877–883.
[7] M.-F. Han, H.-Y. Yin, W.-T. Miao, S. Zhou, Fabrication and properties of anode-supported solid oxide fuel cell, Solid State Ion. 179 (2008) 1545–1548.
[8] C. Johnson, R. Gemmen, N. Orlowskaia, Nano-structured self-assembled LaCrO3 thin film deposited by RF-magnetron sputtering on a stainless steel interconnect material, Compos. Part B: Eng. 35 (2004) 167–172.
[9] B.C.H. Steel, A. Heinzel, Materials for fuel-cell technologies, Nature 414 (2001) 345–352.
[10] J.T.S. Irvine, S. Tao, A stable, easily sintered proton-conducting oxide electrolyte for moderate-temperature fuel cells and electrolyzers, Adv. Mater. 18 (2006) 1581–1584.
[11] H. Li, C. Xia, M. Zhu, Z. Zhou, G. Meng, Reactive Co0.8Sm0.2O1.95 powder synthesized by carbonate co-precipitation: sintering and electrical characteristics, Acta Mater. 54 (2006) 721–727.
[12] D. Ding, B. Liu, M. Gong, X. Liu, C. Xia, Electrical properties of samarium-doped ceria electrolytes of highly active powders, Electrochim. Acta 55 (2010) 4529–4535.
[13] J. Huang, Z. Mao, Z. Liu, C. Wang, Development of novel low-temperature SOFCs with co-ionic conducting SDC–carbonate composite electrolytes, Electrochem. Commun. 9 (2007) 2601–2605.
[14] B. Zhu, X.T. Yang, J. Xu, Z.G. Zhu, S.J. Ji, M.T. Sun, J.C. Sun, Innovative low temperature SOFCs and advanced materials, J. Power Sources 118 (2003) 47–53.
[15] J. Di, M. Chen, C. Wang, J. Zheng, L. Fan, B. Zhu, Samarium doped ceria–(Li(Na)2CO3) composite electrolyte and its electrochemical properties in low temperature solid oxide fuel cell, J. Power Sources 195 (2010) 4695–4699.
[16] J. Huang, Z. Mao, L. Yang, B. Peng, SDC–carbonate composite electrolyte for low-temperature SOFCs, Electrochem. Solid-State Lett. 8 (2005) A437–A440.
[17] J.E. Shemilt, H.M. Williams, Effects of composition and processing method on the low temperature conductivity of samaria-doped ceria electrolytes, J. Mater. Sci. 18 (1999) 1735–1737.
[18] V.V. Kharton, F.M.B. Marques, A. Atkinson, Transport properties of solid oxide electrolyte ceramics: a brief review, Solid State Ion. 135 (2004) 135–149.
[19] N.H. Menzler, F. Tietz, S. Uhenbruck, H.P. Buchkremer, Materials and manufacturing technologies for solid oxide fuel cells, J. Mater. Sci. 45 (2010) 3109–3135.
[20] W. Zhu, C. Xia, D. Ding, X. Shi, G. Meng, Electrical properties of ceria–carbonate composite electrolytes, Mater. Res. Bull. 41 (2006) 2057–2064.
[21] C. Xia, Y. Li, Q. Liu, Z. Wang, L. Jia, Y. Zhao, Y. Li, Intermediate temperature fuel cell with a doped ceria-carbonate composite electrolyte, J. Power Sources 195 (2010) 3149–3154.
[22] A. Boden, J. Di, C. Lagergren, G. Lindbergh, C.Y. Wang, Conductivity of SDC and (Li/Na)2CO3 composite electrolytes in reducing and oxidising atmosphere, J. Power Sources 172 (2007) 520–529.
[23] S.A. Muhammed Ali, A. Muchtar, A.B. Sulong, N. Muhamad, E.N. Majlan, Influence of sintering temperature on the power density of samarium doped-ceria carbonate electrolyte composites for low-temperature solid oxide fuel cells, Ceram. Int. 39 (2013) 5813–5820.
[24] Y. Xia, Y. Bai, X. Wu, D. Zhou, X. Liu, J. Meng, The competitive ionic conductivities in functional composite electrolytes based on the series of M–NLC0.68(Co0.8Sm0.2O1.95), Co0.65(Gd1.85O1.85−δ), Co0.65(Y1.85O1.85−δ), NLC0.53Li2CO3·0.47Na2CO3, Int. J. Hydrogen Energy 36 (2011) 6840–6850.
[25] J. Raharjo, A. Muchtar, W.R.W. Daud, N. Muhamad, E.H. Majlan, Physical and thermal characterisation of SDC–(Li/Na)2CO3 electrolyte ceramic composites, Sains Malays. 41 (2012) 95–102.
[26] X. Zhang, P.D. Hamel, S. Yick, M. Robertson, A study of coarsening samarium doped ceria on interaction with yttria stabilized zirconia, ECS Trans. 35 (2011) 1211–1217.
[27] M.R. Kosinski, R.T. Baker, Preparation and property-performance relationships in samarium-doped ceria nanopowders for solid oxide fuel cell electrolytes, J. Power Sources 196 (2011) 2498–2512.
[28] X. Zhang, C. Deces-Petit, S. Yick, M. Robertson, O. Kesler, R. Maric, D. Ghosh, A study on sintering aids for Sm0.25Co0.75O2+δ electrolyte, J. Power Sources 162 (2006) 480–485.
[29] R. Raza, H. Qin, L. Fan, K. Takeda, M. Mizauhata, B. Zhu, Electrochemical study on co-doped-carbonate composite electrolyte, J. Power Sources 201 (2011) 121–127.
[30] J. Van Herle, A.J. McEvoy, K. Ravindranathan Thampi, Conductivity measurement of various yttria-stabilized zirconia samples, J. Mater. Sci. 29 (1994) 3691–3701.
[31] T. Talebi, M. Haji, B. Raissi, Effect of sintering temperature on the microstructure, roughness and electrochemical impedance of electrophoretically
deposited YSZ electrolyte for SOFCs, Int. J. Hydrogen Energy 35 (2010) 9420–9426.

[32] C. Tongxiang, Z. Yanwei, Y. Shilong, W. Ling, L. Chuanming, Preparation and characterization of Ce0.8Sm0.2O1.9 (SDC)–carbonate composite electrolyte via molten salt infiltration, Mater. Lett. 65 (2011) 2751–2754.

[33] Y. Li, Z.Y. Luo, C.J. Yu, D. Luo, Z.A. Xu, K.F. Cen, The impact of NiO on microstructure and electrical property of solid oxide fuel cell anode, J. Zhejiang Univ. Sci. B 6 (2005) 1124–1129.

[34] C.M. Lapa, F.M.L. Figueiredo, D.P.F. de Souza, L. Song, B. Zhu F.M.B. Marques, Synthesis and characterization of composite electrolytes based on samaria-doped ceria and Na/Li carbonates, Int. J. Hydrogen Energy 35 (2010) 2953–2957.

[35] L. Zhang, R. Lan, C.T.G. Petit, S. Tao, Durability study of an intermediate temperature fuel cell based on an oxide–carbonate composite electrolyte, Int. J. Hydrogen Energy 35 (2010) 6934–6940.

[36] J.B. Huang, Z. Gao, Z.Q. Mao, Effects of salt composition on the electrical properties of samarium-doped ceria/carbonate composite electrolytes for low temperature SOFC, Int. J. Hydrogen Energy 35 (2010) 4270–4275.

[37] R. Gao, Z. Mao, Sintering of Ce0.8Sm0.2O1.9, J. Rare Earths 25 (2007) 364–367.

[38] Y. Ma, X. Wang, H.A. Khalifa, B. Zhu, M. Muhammed, Enhanced ionic conductivity in calcium doped ceria–carbonate electrolyte: a composite effect, Int. J. Hydrogen Energy 37 (2012) 19401–19406.

[39] Z. Gao, J. Huang, Z. Mao, C. Wang, Z. Liu, Preparation and characterization of nanocrystalline Ce0.8Sm0.2O1.9 for low temperature solid oxide fuel cells based on composite electrolyte, Int. J. Hydrogen Energy 35 (2010) 731–737.

[40] Y. Zhao, C. Xia, Z. Xu, Y. Li, Validation of H+O2− conduction in doped ceria–carbonate composite material using an electrochemical pumping method, Int. J. Hydrogen Energy 37 (2012) 11378–11382.