



Preparation of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ fine powders by carbonate coprecipitation for solid oxide fuel cells

Sang Bu Ha, Pyeong-Seok Cho, Yoon Ho Cho, Dokyol Lee, Jong-Heun Lee*

Department of Materials Science and Engineering, Korea University, Anam-dong, Sungbuk-ku, Seoul 136-713, South Korea

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ABSTRACT

A range of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) powders is prepared by the carbonate coprecipitation method for use as anodes in solid oxide fuel cells. The supersaturation ratio ($R = [(\text{NH}_4)_2\text{CO}_3] / ([\text{La}^{3+}] + [\text{Sr}^{2+}] + [\text{Cr}^{3+}] + [\text{Mn}^{2+}])$) during the coprecipitation determines the relative compositions of La, Sr, Cr, and Mn. The composition of the precursor approaches the stoichiometric one at the supersaturation range of $4 \leq R \leq 12.5$, whereas Sr and Mn components are deficient at $R < 4$ and excessive at $R = 25$. The fine and phase-pure LSCM powders are prepared by heat treatment at very low temperature (1000°C) at $R = 7.5$ and 12.5 . By contrast, the solid-state reaction requires a higher heat-treatment temperature (1400°C). The catalytic activity of the LSCM electrodes is enhanced by using carbonate-derived powders to manipulate the electrode microstructures.

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1. Introduction

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) with a perovskite structure has attracted strong attention as a new anode material for solid oxide fuel cells (SOFCs) due to its excellent redox stability, catalytic activity that is able to oxidize methane fuel in the absence of steam, reduced carbon deposition, and high durability against sulfur poisoning [1–3]. LSCM can also be used for the cathode, thereby facilitating fuel cells with a symmetrical structure (LSCM|electrolyte|LSCM) [4,5]. Moreover, the application of LSCM to highly conductive $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) electrolytes as the anode avoids the formation of a resistive interface phase between LSGM and the Ni-based composite anode due to La migration.

The performances of the anode and the cathode in SOFCs are critically dependent on the microstructures of the electrode layer, in particular, the total length of the triple-phase boundary and porosity [6] that, in turn, are determined by the characteristics of the starting powders [7]. When the solid-state reaction is used, prolonged heat treatment at elevated temperature is generally necessary to attain phase-pure LSCM powders due to the sluggish diffusion of various cations. Moreover, the coarsened powders can deteriorate the catalytic activity of the electrode. Thus, the prepara-

tion of fine and phase-pure LSCM powders with less agglomerated configuration is indispensable to improve the electrode performance. In addition, the chemical stability between LSCM and LSGM should be guaranteed for the application in a LSGM-based SOFC.

To date, various chemical routes to prepare LSCM powders have been reported, for example, solid-state reaction [2,4,8–12], glycine nitrate method [3], EDTA (ethylenediaminetetraacetic acid) chelating method [13,14], combustion synthesis [5,15], and gel-casting [7,16]. Nevertheless, the preparation of fine and phase-pure LSCM powders at lower temperatures requires further improvement. Carbonate coprecipitation is a promising and easy chemical route to prepare well-defined and less-agglomerated oxide powders. Li et al. [17] reported that the calcination or sintering temperatures of oxide ceramics such as rare earth oxide-doped ceria, $\text{Y}_3\text{Al}_5\text{O}_{12}$ [18] and MgAl_2O_4 [19] can be markedly decreased by using carbonate precipitation or coprecipitation. The present authors [20] have reported that lowering of the sintering temperature using carbonate coprecipitation is also valid for the LSGM electrolyte. In this study, LSCM powders are prepared, for the first time, via carbonate coprecipitation. The phase-pure and fine LSCM powders are prepared at 1000°C , whereas a significantly higher temperature (1400°C) is required in the solid-state reaction. The principal parameters to determine the cation composition, the phase purity of the powders and the compositional uniformity of the precursors are systematically investigated with variation of coprecipitation methods, the degree of supersaturation, and heat-treatment schedules.

* Corresponding author. Tel.: +82 2 3290 3282; fax: +82 2 928-3584.
E-mail address: jongheun@korea.ac.kr (J.-H. Lee).

2. Experimental

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{Sr}(\text{NO}_3)_2$ (99+%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, all from Sigma–Aldrich, Inc., USA, were used as the source materials. Most of the carbonate precursors were prepared by the ‘reverse strike’ method (the addition of the mixed source solution to the precipitant solution) to achieve a more uniform cation distribution by instantaneous precipitation. Stoichiometric amounts of each component of LSCM were dissolved in distilled water, after which 200 ml of a mixed aqueous solution ($[\text{La}^{3+}] = 0.075 \text{ M}$, $[\text{Sr}^{2+}] = 0.025 \text{ M}$, $[\text{Cr}^{3+}] = 0.05 \text{ M}$, $[\text{Mn}^{2+}] = 0.05 \text{ M}$) was dripped (dripping speed: 5 ml per min) into 200 ml of $(\text{NH}_4)_2\text{CO}_3$ aqueous solution. During the precipitation, the solution was stirred mildly and the temperature was kept at 70°C . The degree of supersaturation during coprecipitation was controlled by varying the ratio of the precipitant concentration to the total concentration of metal cations ($[(\text{NH}_4)_2\text{CO}_3]/([\text{La}^{3+}] + [\text{Sr}^{2+}] + [\text{Cr}^{3+}] + [\text{Mn}^{2+}])$), which is defined as the supersaturation ratio, R , from 1.5 to 25.0. In order to investigate the effect of the ‘reverse strike’ method, the carbonate precursors were also prepared by ‘normal strike’ (the addition of precipitant solution to the mixed source solution). The precipitates were washed with distilled water and ethanol, and then dried for 24 h under a nitrogen atmosphere at room temperature. After pulverization, the precipitates were calcined at $800\text{--}1200^\circ\text{C}$ for 2 h.

The LSCM powders were also prepared by conventional solid-state reaction for comparison. For this, stoichiometric amounts of La_2O_3 , SrCO_3 and Cr_2O_3 powders (all 99.9%, High Purity Chemicals, Inc., Japan) and Mn_2O_3 powder (99%, Aldrich, Inc., USA) were ball-milled in ethanol for 24 h. After drying and pulverization, the precursors were calcined at $800\text{--}1400^\circ\text{C}$ for 2 h. The powder compositions were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 4300 DV, Perkin Elmer, USA).

The LSGM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$) powders were prepared by the glycine nitrate method using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Kanto Chemical Co., Inc., Japan), $\text{Sr}(\text{NO}_3)_2$ (99.995%, Aldrich, Inc., USA), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.999%, High Purity Chemicals, Inc., Japan) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999%, Aldrich, Inc., USA) according to Ref. [21]. The same weights of LSGM (calcined at 1400°C for 4 h) and LSCM powders were mixed by mortar and then heat-treated at $1100\text{--}1300^\circ\text{C}$ for 3 h in order to check the chemical compatibility between LSGM and LSCM. The reaction between LSGM and LSCM powders was examined by X-ray diffraction (XRD) analysis. A symmetric LSCM|LSGM|LSCM cell was fabricated by the screen printing of the LSCM pastes on LSGM sintered pellets (diameter: 12 mm), and subsequent heat treatment at 1100°C for 1 h. The electrochemical activity for O_2 reduction was evaluated by measuring the impedance of the cell at 700°C in air by means of an impedance analyzer (Alpha-N, Novo control, Germany).

3. Results and discussion

The cation composition of the powders prepared by the ‘reverse strike’ method was examined at the various supersaturation ratios (R) (Fig. 1). The concentrations of La, Sr, and Mn determined from ICP-AES analyses are normalized with respect to that of Cr because the Cr component is most abundant over the entire range of R values. In addition, the doping concentration ($[\text{Sr}]$) of the A-site cation in the ABO_3 perovskite structure is normalized again by that of the host A-site cation ($[\text{La}]$) (Fig. 1(d)). The dotted line in Fig. 1(a)–(d) corresponds to the stoichiometric composition of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$. The $[\text{La}]/[\text{Cr}]$ ratio remains similar (1.26–1.40) at $1.5 \leq R \leq 12.5$ and increases to 1.70 at $R = 25.0$ (Fig. 1(a)). By contrast, the $[\text{Sr}]/[\text{Cr}]$ and $[\text{Mn}]/[\text{Cr}]$ ratios, as well

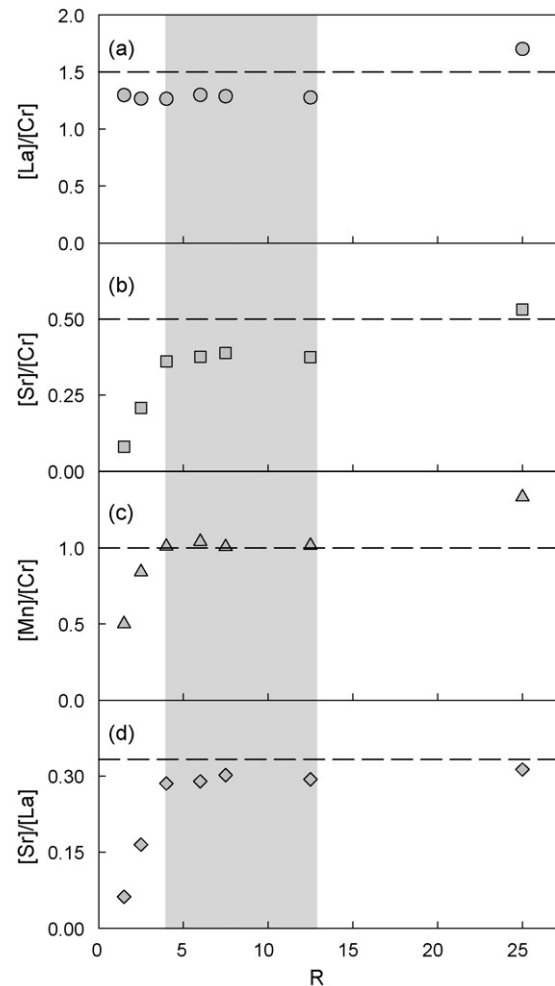


Fig. 1. Relative compositions of the powders as a function of R : (a) $[\text{La}]/[\text{Cr}]$, (b) $[\text{Sr}]/[\text{Cr}]$, (c) $[\text{Mn}]/[\text{Cr}]$ (normalized by $[\text{Cr}]$) and (d) $[\text{Sr}]/[\text{La}]$ (normalized by $[\text{La}]$).

as the ratios between the A-site cations ($[\text{Sr}]/[\text{La}]$), increase as R is increased from 1.5 to 4 and tend to saturate at $4.0 \leq R \leq 12.5$ (Fig. 1(b)–(d)). With further increase in R to 25.0, the $[\text{Sr}]/[\text{Cr}]$ and $[\text{Mn}]/[\text{Cr}]$ ratios exceed the stoichiometric composition. These results indicate that moderate supersaturation ($R \geq 4.0$) is necessary to precipitate Sr and Mn components, whereas La and Cr components can be precipitated even at relatively low supersaturation. It is concluded that the deficiency and the excess of La, Sr, and Mn components at $R < 4.0$ and $R \geq 25.0$, respectively, hamper the formation of single-phase LSCM. Considering the balance between all the cations, the supersaturation range of $4.0 \leq R \leq 12.5$ can be regarded as the best R window for carbonate coprecipitation (grey shaded area in Fig. 1).

The phase evolution of the powders was studied according to variation in the calcination temperature (CT) (Fig. 2). When the precursors are precipitated at $R = 25.0$, the La_2O_3 phase is formed as the minor phase and is attributed to an increase of $[\text{La}]/[\text{Cr}]$ beyond the stoichiometric composition at $R = 25.0$ (Fig. 2(g)–(i)). At $R = 4.0$, although the LSCM phase is attained by heat treatment at $< 1000^\circ\text{C}$ (Fig. 2(a)), LaCrO_4 remains as the second phase at $\leq 1100^\circ\text{C}$ (Fig. 2(b)) and the phase-pure LSCM phase is attained at $\geq 1200^\circ\text{C}$ (Fig. 2(c)). The minimum temperature to achieve phase-pure LSCM phase is decreased significantly to 1000°C at $R = 7.5$ (Fig. 2(e)). These results demonstrate that fine-tuning of R is necessary to decrease the formation temperature of phase-pure LSCM.

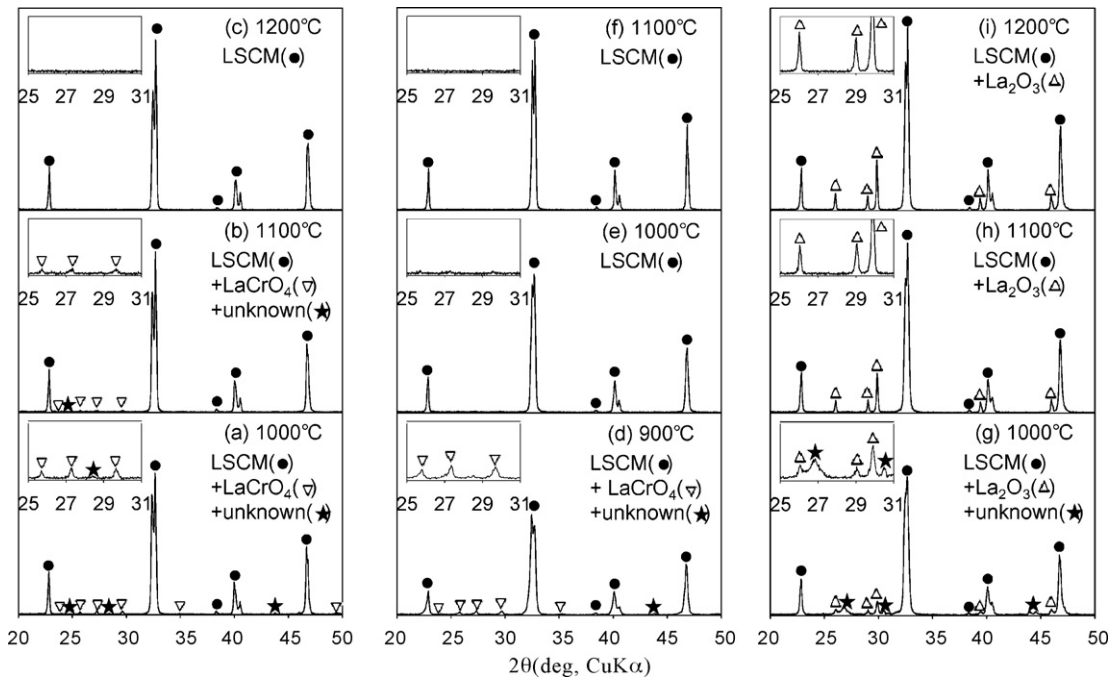


Fig. 2. X-ray diffraction (XRD) patterns of the powders prepared by 'reverse strike' route as a function of supersaturation ratio (R) during precipitation and calcination temperature (CT): (a) $R=4.0$, CT = 1000 °C; (b) $R=4.0$, CT = 1100 °C; (c) $R=4.0$, CT = 1200 °C; (d) $R=7.5$, CT = 900 °C; (e) $R=7.5$, CT = 1000 °C; (f) $R=7.5$, CT = 1100 °C; (g) $R=25.0$, CT = 1000 °C; (h) $R=25.0$, CT = 1100 °C; and (i) $R=25.0$, CT = 1200 °C (all precursors are calcined at CT for 2 h).

By contrast, the powders prepared by solid-state reaction contain the $Mn_{1.5}Cr_{1.5}O_3$ and unknown second phases, even at a heat-treatment temperature of 1300 °C (Fig. 3(b)), and phase-pure LSCM powders are attained at ≥ 1400 °C (Fig. 3(c)). The high CT and long reaction time are attributed to the sluggish diffusion of La, Sr, Cr, and Mn cations via the contact points between two different particles.

The effect of the precipitation method was also investigated. The precursors attained by the 'normal strike method' at $R=7.5$ are converted into phase-pure LSCM at ≥ 1200 °C (Fig. 3(f)). At the same

supersaturation, the change of precipitation mode from 'reverse strike' to 'normal strike' increases the heat-treatment temperature required to attain phase-pure LSCM from 1000 to 1200 °C. Considering the cation composition at various R values in Fig. 1, it is feasible that the La and Cr components precipitate at the initial stage, but the Sr and Mn components at the late stage, when the 'normal strike' method is used. The separate precipitation of different cations during 'normal strike' precipitation can therefore be regarded as the main reason for the high heat-treatment temperature.

Strictly speaking, the precipitations of the Sr and Mn components next to those of La and Cr would also be valid in the 'reverse strike' route. When, however, the mixed source solution was dropped into a highly concentrated solution of precipitant, the various cations within each droplet would have precipitated almost instantaneously. This would have induced a more homogeneous cation distribution in the precursors that, in turn, would have decreased the formation temperature for phase-pure LSCM. Li et al. [22] prepared the carbonate precursors of YAG ($Y_3Al_5O_{12}$) from a mixed solution of ammonium aluminum sulfate dodecahydrate

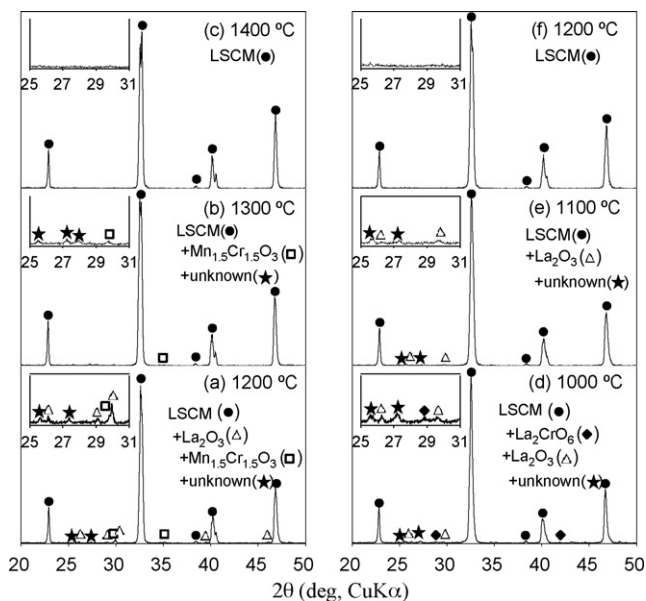


Fig. 3. X-ray diffraction (XRD) patterns of powders prepared by (a), (b), and (c) solid-state reaction (SSR) and (d), (e), and (f) 'normal strike' (NS) route at $R=7.5$ as a function of calcination temperature (CT): (a) SSR, CT = 1200 °C; (b) SSR, CT = 1300 °C; (c) SSR, CT = 1400 °C; (d) NS, CT = 1000 °C; (e) NS, CT = 1100 °C; and (f) NS, CT = 1200 °C.

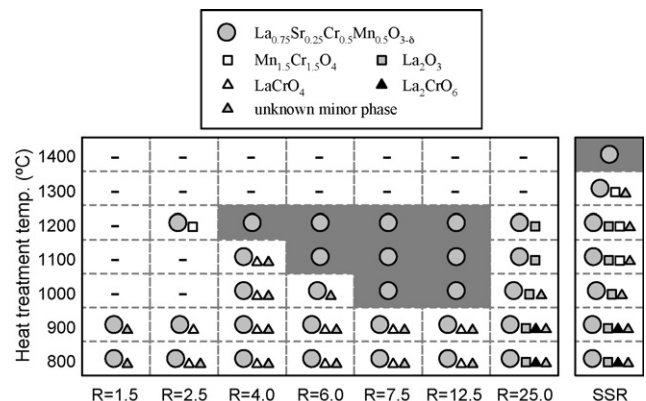


Fig. 4. Phase evolution of powders as a function of supersaturation ratio (R) according to precipitation and calcination temperature (CT).

and yttrium nitrate hexahydrate using ammonium hydrogen carbonate as the precipitant. The pure YAG phase could be prepared from the calcination of precursors at 1000 °C when the 'reverse strike' method was used, while even heat treatment at 1500 °C was insufficient for such preparation using the 'normal strike' precipitation. Based on the present results, this CT lowering effect by using the 'reverse strike' method is attributed to enhancement of cation homogeneity.

The phase evolution of the precursors was examined as a function of CT and R value (Fig. 4). The phase-pure LSCM fine powders can be prepared by calcination at 1000 °C at $R=7.5$ and 12.5, while the minimum CT for the preparation of pure LSCM powders is increased to 1100 and 1200 °C as R is decreased to 6.0 and 4.0, respectively. Thus, the supersaturation range of $7.5 \leq R \leq 12.5$ is considered the optimum part of the approximate R window ($4.0 \leq R \leq 12.5$) for LSCM formation, as shown in Fig. 1.

The morphologies of the LSCM powders prepared at $R=7.5$ using the 'reverse strike' method were examined with scanning electron microscopy (SEM) (Fig. 5). The LSCM powders prepared by carbonate coprecipitation consist of uniform particles with a less agglomerated configuration. The average particle size of the LSCM powders calcined at 1000 and 1100 °C is approximately 250 and 410 nm, respectively (Fig. 5(a) and (b)). By contrast, the LSCM powders prepared by solid-state reaction show coarse particles (average particle size: $\sim 1.6 \mu\text{m}$), probably due to the elevated CT (1400 °C) (Fig. 5(c)).

The LSCM powders can be applied to various electrolytes such as yttria-stabilized zirconia [1–5,7,8,10,12,16,23–31], scandia-stabilized zirconia [32], and LSGM [9,11,13–15,33,34] as the cathode or anode in SOFCs. Of these three electrolytes, LSGM is most promising with similar thermal expansion [2,35] and primitive cell volume [2,36] to LSCM electrodes. Although slight inter-diffusion between perovskite components (e.g., La and Sr) can improve the bonding strength at the electrolyte|electrode interface [2], substantial interdiffusion of various cations between the electrolyte and electrode might lead to the formation of a resistive interface phase, which eventually deteriorates the fuel cell performance.

In order to investigate the chemical compatibility between the electrolyte and electrode, the LSCM powders ($R=7.5$) in the present study were mixed with LSGM powders and heat-treated at various temperatures. The LSCM powders prepared by solid-state reaction and heat treatment at 1400 °C (denoted as LSCM-SSR-1400) do not react with LSGM at 1100 and 1200 °C (Fig. 6(a) and (b)), but do at 1300 °C (Fig. 6(c)). Huang et al. [15,34] studied the reaction between LSCM powders prepared by combustion synthesis and LSGM powders prepared by solid-state reaction. The mixture between LSGM and LSCM powders began to react at 1300 °C, which is consistent with the present results. The LSCM powders prepared by the calcination of carbonate precursors at 1100 °C (LSCM-1100) remain unreacted at 1100 °C and begin to react at 1200 °C, whereas those prepared at 1200 and 1300 °C (LSCM-1200 and LSCM-1300) remain unreacted at 1200 °C and begin to react at 1300 °C. This is attributed to the ability of the finer LSCM particles with higher activity to react more easily with the LSGM powders. Thus, the heat-treatment temperature should be determined in accordance with the CT in order to maintain the fine microstructures within the LSCM electrode layer without significant reaction with the LSGM electrolytes.

The catalytic activity of the electrode was examined by measuring the complex impedance of the LSCM|LSGM|LSCM symmetric cell at 700 °C in air (Fig. 7). The impedance is halved due to the symmetric configuration to calculate the electrode polarization resistance for one electrode. For this measurement, various LSCM powders were prepared in the form of paste, applied to the LSGM sintered body, and then heat-treated at 1100 °C. The typical cathodic polarization resistance of LSCM on YSZ ranges from 0.5 to 2.5 $\Omega \text{ cm}^2$ at 900 °C [16]. In the present study, the electrode

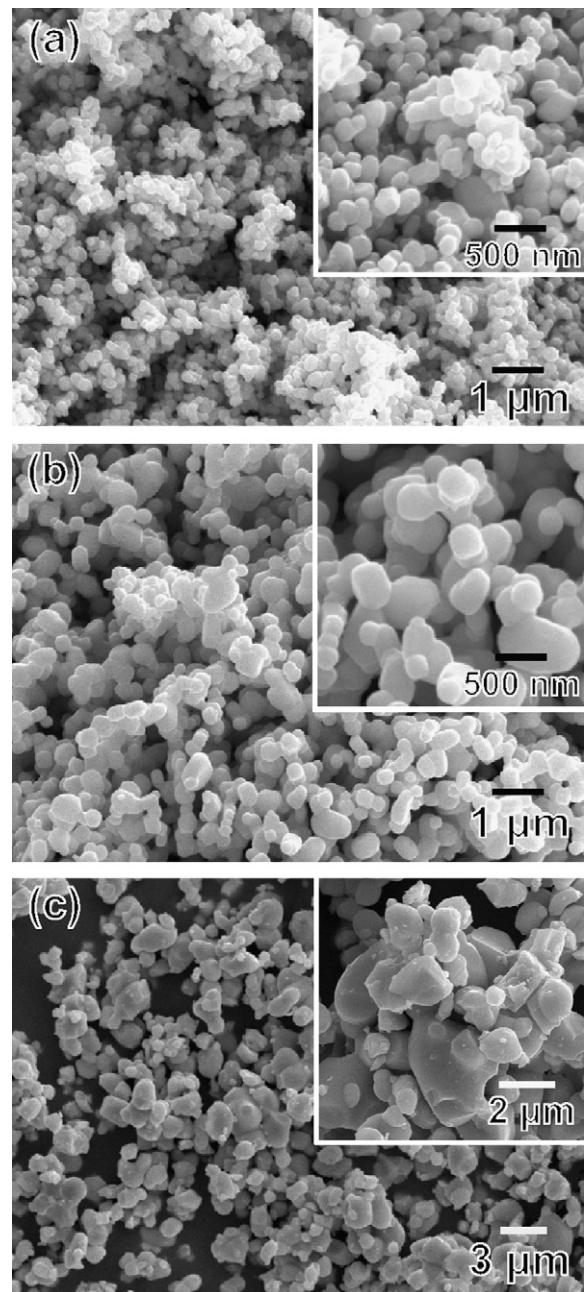


Fig. 5. Scanning electron microscopy (SEM) images of LSCM powders prepared by 'reverse strike' precipitation at $R=7.5$ and solid-state reaction: (a) 'reverse strike' precipitation, calcined at 1000 °C for 2 h; (b) 'reverse strike' precipitation, calcined at 1100 °C for 2 h; and (c) solid-state reaction, calcined at 1400 °C for 2 h.

polarization is relatively large because the measuring temperature is low (700 °C) and the electrode microstructure is not fully optimized. Nevertheless, the results showed a consistent tendency. The electrode polarization at 700 °C in air is highest in the LSCM-SSR-1400/LSGM/LSCM-SSR-1400 cell and becomes smaller when the electrodes are fabricated using carbonate-derived LSCM powders. As expected, the LSCM-1100/LSGM/LSCM-1100 cell shows the lowest electrode polarization resistance (10.03 $\Omega \text{ cm}^2$), which is attributed to an increase of the triple-phase boundary due to the finer LSCM particles.

The results of this study demonstrate that the catalytic activity of the LSCM electrode can be designed by controlling the particle size and porosity in the LSCM electrode layers. The particle sizes within the LSCM electrode layers can be manipulated during the

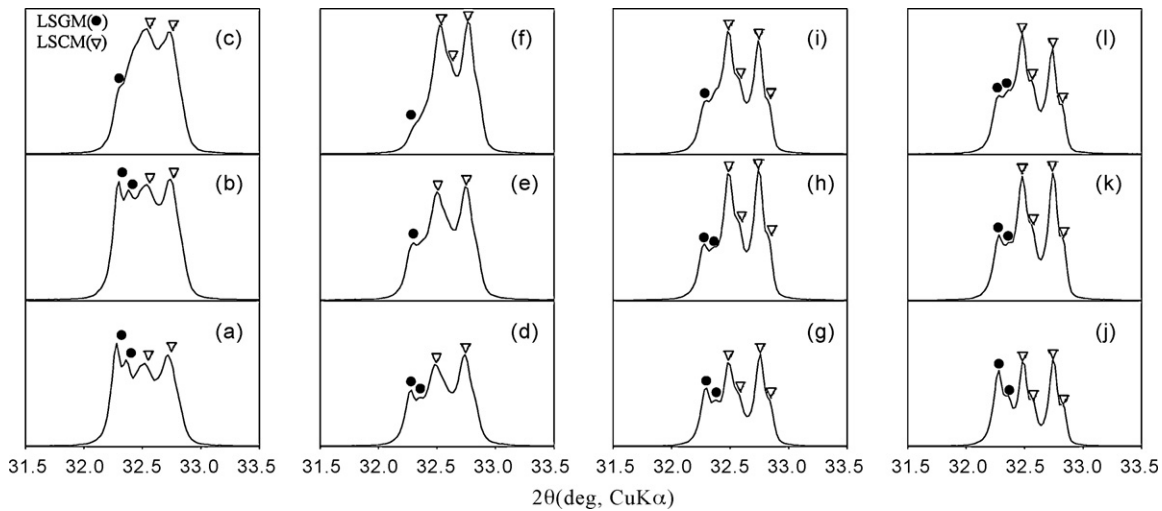


Fig. 6. X-ray diffraction (XRD) patterns of mixed powders heat-treated at 1100–1300 °C for 3 h: mixture between LSCM-SSR-1400 (prepared by solid-state reaction and calcination at 1400 °C for 2 h) and LSGM powders heat-treated at (a) 1100 °C, (b) 1200 °C and (c) 1300 °C for 3 h; mixture between LSCM-1100 (prepared by carbonate coprecipitation at $R=7.5$ and calcination at 1100 °C for 2 h) and LSGM powders heat-treated at (d) 1100 °C, (e) 1200 °C and (f) 1300 °C for 3 h; mixture between LSCM-1200 (prepared by carbonate coprecipitation at $R=7.5$ and calcination at 1200 °C for 2 h) and LSGM powders heat-treated at (g) 1100 °C, (h) 1200 °C and (i) 1300 °C for 3 h; and mixture between LSCM-1300 (prepared by carbonate coprecipitation at $R=7.5$ and calcination at 1300 °C for 2 h) and LSGM powders heat-treated at (j) 1100 °C, (k) 1200 °C and (l) 1300 °C for 3 h.

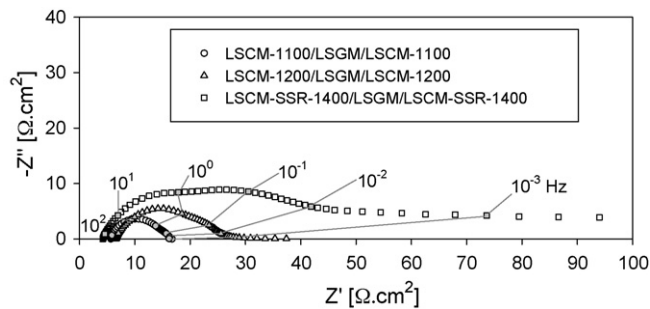


Fig. 7. Complex impedance spectra of various symmetric LSCM|LSGM|LSCM cells at 700 °C in air. Impedance halved due to symmetric configuration to calculate electrode polarization resistance for one electrode.

calcination and heat treatment by using the finer and more phase-pure LSCM powders prepared by carbonate coprecipitation. This is very important in maximizing the length of the triple-phase boundaries at the anode or cathode, which serve to decrease the electrode polarization during SOFC operation.

4. Conclusion

Phase-pure and fine $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) powders have been prepared by carbonate coprecipitation. A composition close to the stoichiometric value can be attained by controlling the supersaturation ratio ($R = [(\text{NH}_4)_2\text{CO}_3] / ([\text{La}^{3+}] + [\text{Sr}^{2+}] + [\text{Cr}^{3+}] + [\text{Mn}^{2+}])$) during coprecipitation. The lowest heat-treatment temperature able to attain pure LSCM phase is 1000 °C when the carbonate precursor is prepared by the ‘reverse strike’ method (the addition of the mixed source solution to the precipitant solution), compared with 1200 °C when prepared by the ‘normal strike’ (the addition of precipitant solution to the mixed source solution) method, and 1400 °C when the solid-state reaction is employed. Instantaneous precipitation of four different cations under the well-tuned supersaturation ratio of $7.5 \leq R \leq 12.5$ is the key to the preparation of fine and phase-pure LSCM powders at low temperature using carbonate coprecipitation. The catalytic activity of the electrode is significantly improved by using carbonate-derived LSCM powders.

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