

SYNTHESIS AND CHARACTERIZATION OF LANTHANUM STRONTIUM COBALTITE POWDER USING A COMBINED CHEMICAL AGENT FOR PROTON CONDUCTING SOFC

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ABSTRACT

A modified sol-gel synthesis route was applied in the preparation of a single perovskite phase of lanthanum strontium cobaltite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCO) for cathode application in proton conducting solid oxide fuel cell (SOFC). In this process, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) have been used as a combined chelating agent, while ethylene glycol (EG) and activated carbon (AC) have been used as a combined surfactant/dispersing agent. The amounts of AC to EG have been varied and the synthesized powders were characterized by X-ray diffractometer (XRD), particle size analyzer (PSA) and field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX) spectrometer. XRD results confirmed that a single LSCO perovskite phase formed at temperatures of 900 °C and 1000 °C. PSA and FESEM results revealed that the average particle size diameter of the produced powders increased as the ratio of AC:EG increased. The smallest average particle size diameters (19 nm) was obtained at 900 °C with ratio of 1:3 (AC:EG). EDX results showed that the calculated mole fraction of each element (La, Sr, Co) in the single phase powders were relatively closed to their nominal mole fraction, except for Sr. It can be concluded that the ratio of AC:EG affects the phase formation and average particle size diameter of LSCO powder.

Keywords: LSCO; cathode; modified sol-gel; chemical agent

INTRODUCTION

Nowadays, development of solid oxide fuel cell (SOFC) has been focused to lower the operating temperature from high (800 - 1000 °C) to intermediate (500 - 750 °C)

temperatures range. At the reduced temperatures, proton-conducting SOFC (H^+ -SOFC) has some remarkable advantages compared with oxygen ion-conducting SOFC (O^{2-} -SOFC). Proton conductors such as strontium cerium oxide, $SrCeO_3$ and barium zirconium oxide, $BaZrO_3$ have lower activation energy than oxygen ion conductors such as yttria-stabilized zirconia (YSZ), indicating that ionic conductivity of proton conductors is higher than oxygen ion conductors at intermediate temperatures. Additionally, H^+ -SOFC produces water at cathode side, avoiding the dilution of fuel and the fuel remains pure [1, 2]. However, increase in electrode overpotential, mainly cathode overpotential becomes the main problem for H^+ -SOFC [3, 4].

To solve the problem, development of a superior cathode becomes an important subject. A good cathode material should have high catalytic activity and conductivity, and good compatibility with working electrolyte [4]. Generally, the properties of materials are affected by the way how it is produced. Thus, optimizing cathode properties such as its microstructure by controlling the synthesis parameters is one of the promising ways to achieve the goal [5]. Production of ultra-fine cathode particles will reduce the cathode overpotential as it offers a large surface area and extends reaction sites at cathode/electrolyte interface [6]. In this present work, lanthanum strontium cobaltite, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSCO), a material for cathode candidate has been prepared via a modified sol-gel method. Two chemicals namely ethylene glycol (EG) and activated carbon (AC) which act as surfactant and dispersing agent, respectively have been employed as a combined chemical agent. They help to control the particle size by breaking the agglomeration in the synthesized powder. The effect of the combined and a single chemical agent on the phase formation and microstructure of the produced LSCO powders has been analyzed and reported.

MATERIALS AND METHOD

Synthesis of powder.

Analytical grade of metal nitrate salts of lanthanum, $La(NO_3)_3 \cdot 6H_2O$ (99.995% purity, ACROS), strontium, $Sr(NO_3)_2$ (99+% purity, ACROS) and cobalt, $Co(NO_3)_2 \cdot 6H_2O$ (99% purity, ACROS) were used as precursor materials to produce $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSCO) powder via a modified sol-gel method. A mixture of these precursor materials was firstly dissolved in 100 mL deionized water. Then, calculated amounts of citric acid, CA (99.5% purity, MERCK) and ethylenediaminetetraacetic acid, EDTA (99% purity, ACROS) were slowly added into the solution mixture, accordingly. After that, the pH of the solution was adjusted to be 0.5. Finally, the respective amounts of EG/AC as shown in Table 1 was added, and the solution was continuously stirred and heated for several hours to obtain a viscous gel. The resulting viscous gel was dried at 150 °C and 250 °C, accordingly. The as-synthesized powder was calcined at 700, 800, 900 and 1000 °C with a heating/cooling rate of 5 °C min⁻¹ and soaked for 5 hours. Details for the production of the LSCO powders were described elsewhere [7].

Table 1: Molar ratio of AC to EG as a combined chemical agent

Molar ratio of EG	Molar ratio of AC	Sample denotation
3	1	A
3	2	B
3	3	C

Characterization of powder.

An X-ray diffractometer (XRD, Bruker D8 Advance) using a monochromatic Cu-K α radiation source ($\lambda = 0.1540$ nm) with Ni-filtered was used to confirm the phase formation of LSCO perovskite powder. The XRD was operated at 40 kV and 40 mA for the 2 theta (θ) ranging from 20° to 80°. The percentage of perovskite phase present in the calcined powders was calculated using Eq. 1:

$$\text{Perovskite phase} = \frac{I_p}{I_p + I_m} \times 100\% \quad (1)$$

where I_p is the maximum intensity of the perovskite phase and I_m is the maximum intensity of the impurity phases. Morphology of the calcined powders was examined by a Merlin Compact Zeiss field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX) spectrometer. The imaging was performed in secondary electron mode using an accelerating voltage of 15 kV at magnifications 50000 $\times$. Particle size distribution analysis of the powders was done using a Nano-ZS particle size analyzer (PSA) manufactured by Malvern using deionized water as a dispersant.

RESULTS AND DISCUSSION

Phase Formation Analysis

A single LSCO perovskite phase formation was confirmed by XRD measurements as shown in figure 1. The strongest peaks in all XRD patterns were matched with Joint Committee of Powder Diffraction Standards (JCPDS) file 48-0121 with a cubic structure (Pm-3m). The pronounced peaks can be indexed using the following Miller indices (hkl): (100), (110), (111), (200), (211), (220), (300) and (310). From the XRD patterns, it can be seen that a single LSCO perovskite phase was formed at calcination temperatures of 900 °C and 1000 °C using surfactant/dispersing agent (EG/AC) as a combined chemical agent. The results are comparable to our previous work [8] which reported that a single LSCO perovskite phase was also formed at calcination temperature of 900 °C using a single surfactant (EG) and a single dispersing agent (AC). The results are also comparable to the reported works done by Tao et al [9] and Bansal and Zhong [10] for production of a single LSCO perovskite phase via citrate-

EDTA method and solution combustion method, respectively. A summary of XRD analysis is shown in Table 2.

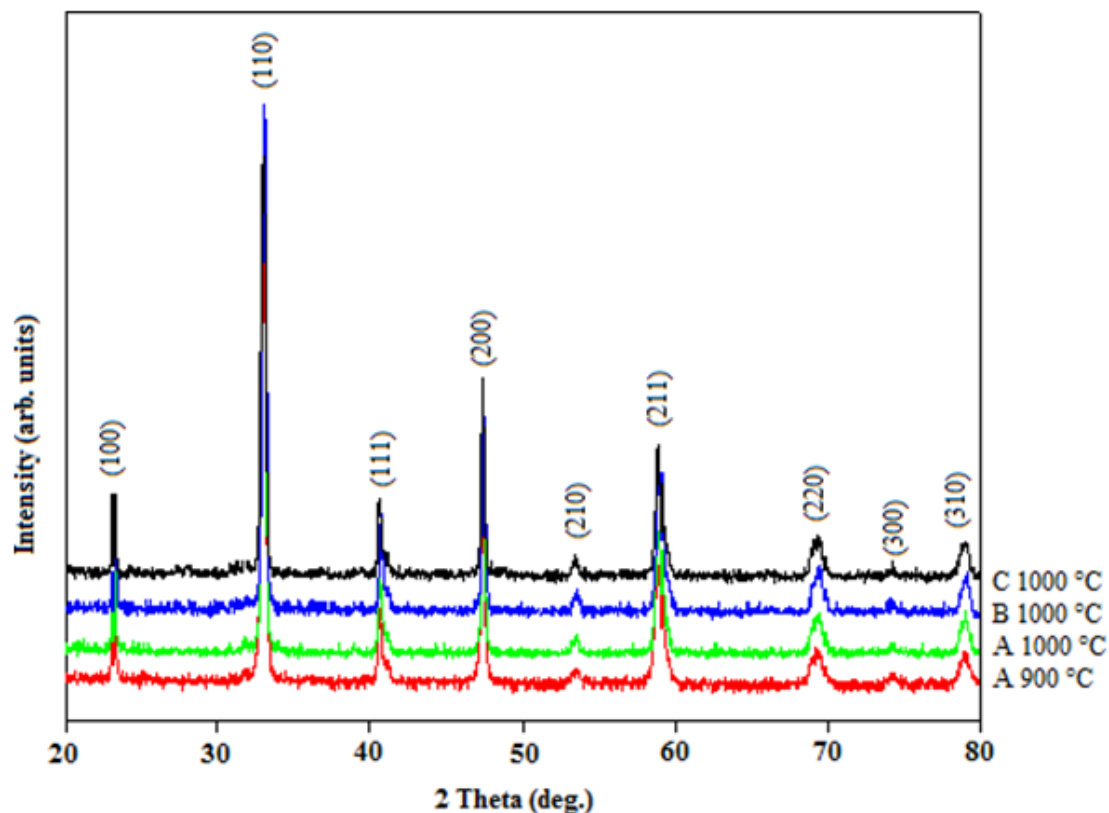


Figure 1: XRD patterns of the single LSCO perovskite phase powders prepared using a combined chemical agent

Table 2: A summary of XRD analysis of the prepared powders at different calcination temperatures

Sample	Calcination temperature (°C)	Percentage of <u>perovskite phase</u> (%)
A	700	80.62
	800	91.43
	900	100.00
	1000	100.00
B	700	67.41
	800	85.33
	900	95.18
	1000	100.00
C	700	77.39
	800	81.62
	900	93.44
	1000	100.00
Single EG	900	100.00
Single AC	900	100.00

Morphology and Particle Size Analysis

Figure 2 depicts FESEM images showing the morphology of the single perovskite phase LSCO powders prepared with different amount of AC to EG, and obtained at different calcination temperatures. The powders consist of homogeneous and almost identical particles. The particles formed porous network and connected with each other. Figure 3 represents EDX spectrum of A900 powder. The spectrum shows the presence of lanthanum (La), strontium (Sr), cobalt (Co), oxygen (O) and carbon (C) in the A900 powder. EDX spectra of other powders (A1000, B1000 and C1000) also showed the same observation as A900 powder. The elemental composition distribution analysis of the single phase powders is presented in the Table 3. It can be seen that the calculated mole fraction obtained from EDX measurement for Sr is slightly deviated to the less value from its nominal mole fraction. It might be due to the leaching of Sr in the samples, giving rise to the fluctuations of chemical composition. The residual carbon content might be due to the incomplete removal of carbon from the AC used in the preparation of the LSCO powders.

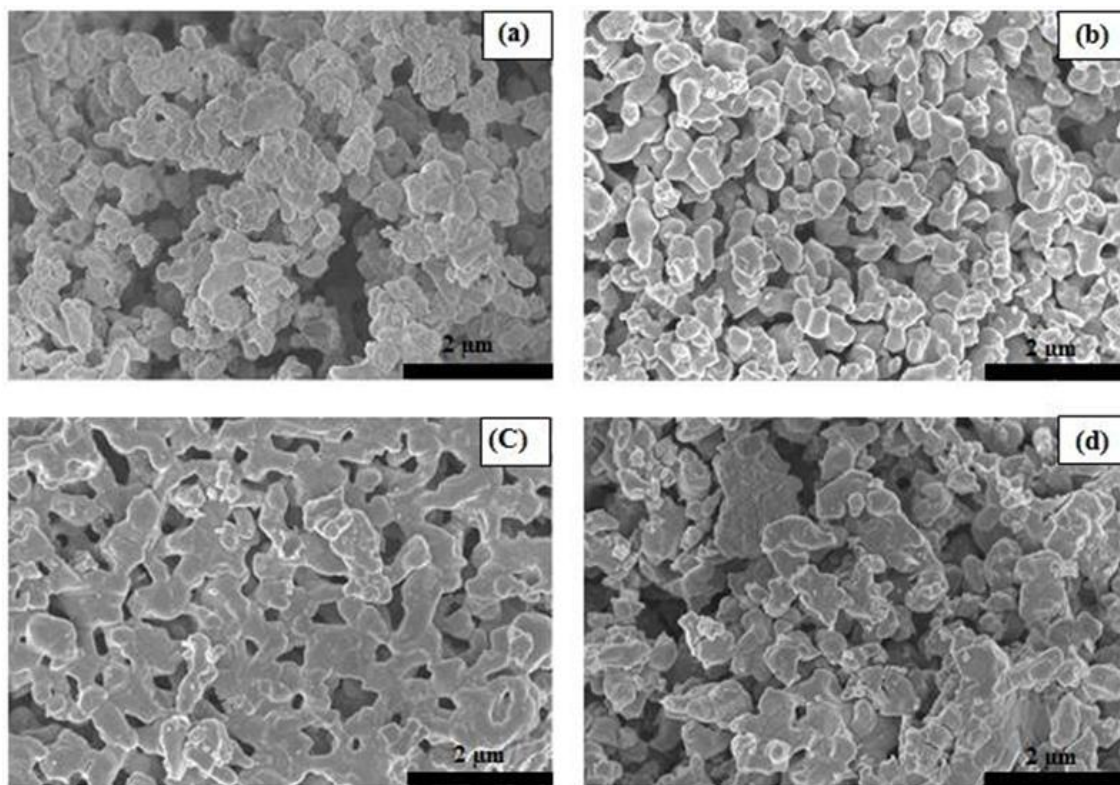


Figure 2: SEM images of (a) A 900; (b) A 1000; (c) B 1000 and (d) C 1000 powders

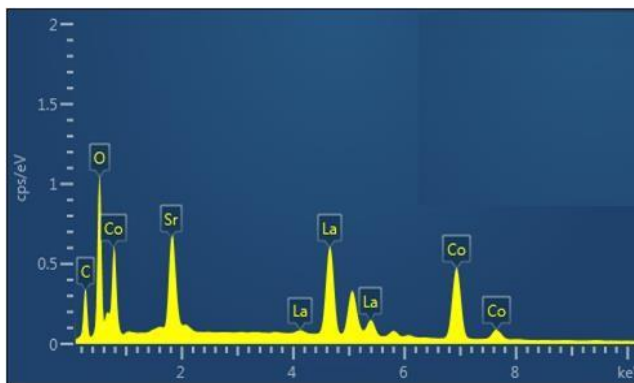


Figure 3: EDX spectrum of A 900 powder

Table 3: EDX data of the single phase powders

Sample	Element										
	wt%					Nominal mole fraction			Calculated mole fraction		
	La	Sr	Co	O	C	La	Sr	Co	La	Sr	Co
A900	43.45	11.25	29.44	11.99	3.87				0.62	0.26	1.00
A1000	38.58	10.62	23.56	15.83	11.41	0.60	0.40	1.00	0.69	0.30	1.00
B1000	34.56	11.64	24.32	15.34	14.14				0.60	0.32	1.00
C1000	39.98	9.78	25.09	15.46	9.70				0.67	0.26	1.00

Table 4 shows the comparison of average particle size diameter of powders prepared with a combined and a single chemical agent. It is clearly seen that the particle size is significantly decreased when the combined surfactant/dispersion agent was employed in producing the powder. It has smaller particle size compared to those prepared using a single surfactant and a single dispersing agent. It is also clearly seen that the particle size of powders prepared using a combined chemical agent increased with increasing of AC to EG ratio. The discrepancy between the results might be due to the different properties of the surfactant and dispersion agent employed as they have different molecular structure and different relative bond strength towards metal cations during synthesizing process. Additionally, the reaction mechanism of both surfactant and dispersion agent might be different as they work as a single and as a combined chemical agent. A detail study on the reaction mechanism is in progress and will be reported elsewhere.

Table 4: Average particle size diameter

Sample	Element										
	wt%					Nominal mole fraction			Calculated mole fraction		
	La	Sr	Co	O	C	La	Sr	Co	La	Sr	Co
A900	43.45	11.25	29.44	11.99	3.87				0.62	0.26	1.00
A1000	38.58	10.62	23.56	15.83	11.41				0.69	0.30	1.00
B1000	34.56	11.64	24.32	15.34	14.14	0.60	0.40	1.00	0.60	0.32	1.00
C1000	39.98	9.78	25.09	15.46	9.70				0.67	0.26	1.00

CONCLUSION

LSCO powder was successfully prepared using a modified sol-gel method by employing ethylene glycol (EG) and activated carbon (AC) as a combined surfactant/dispersing agent. A single perovskite phase of the LSCO was obtained at calcination temperatures of 900 °C and 1000 °C. The produced single phase powders consist of homogenous particles. The employment of the combined surfactant/dispersion agent significantly reduces the particle size as the produced powder has smaller particle size as compared to those which have been prepared using single surfactant and dispersion agent, respectively. Powders prepared with 1:3 ratio of AC to EG has the smallest particle size which is ~ 19 nm. The outcomes from this study are expected to embark a significant knowledge in optimizing the microstructure of sample in order to produce better cathode properties for better performance of intermediate temperature H⁺-SOFC.

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