Thermal decomposition, phase formation and microstructure analysis of surfactant assisted sol-gel derived La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ material

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Abstract. A single-phase of perovskite-type oxide material can be prepared at a processing temperature relatively lower than 1000 °C through a sol-gel method. However, it is affected by the nature of chemical additives employed during the synthesis process. In the present work, sol-gel derived lanthanum strontium cobaltite, La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC64) material is prepared using various non-ionic surfactants namely polyoxyethylene (10) oleyl ether (Brij-97), polyoxyethylene octyl phenyl ether (Triton-X-100) and polyoxyethylene (20) sorbitan monooleate (Tween-80). The prepared powders of the LSC material is subsequently subjected to the thermal decomposition, phase formation and microstructure analysis by a thermal gravimetric analyzer, an X-ray diffractometer and a scanning electron microscope (SEM), respectively. The as-synthesized powders are calcined at different temperatures based on the thermal gravimetric analysis results. X-ray diffractometer results reveal that all of the calcined powders consist of more than 90 % perovskite phase of LSC64 and other secondary phases such as cobalt oxide, lanthanum oxide and strontium carbonate. The Brij-97-based and Tween-80-based calcined powders have morphology of typical clump-like network structure, while the Triton-X-100-based calcined powder has morphology of flake-like network structure.

1. Introduction

Perovskite-type oxide cobalt (Co) containing materials are well-known to have good electrical conductivity and excellent thermoelectric properties. This material is practically being used as cathode material for the application of solid oxide fuel cell (SOFC), an electrochemical device that converts chemical energy directly into electricity. One of the Co containing materials is strontium-doped lanthanum cobaltite, La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, LSC (0 ≤ x ≤ 0.9). LSC with x = 0.4, La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC64) attracts greater attention as it has better electrochemical properties than the others particularly for the application of SOFC [1–3]. However, its electrochemical performance depends on its powder
properties such as powder purity, phase structure and microstructure. Ultrafine and high purity perovskite phase powder with cubic structure is usually desirable for high performance SOFC device. The powder can be produced by controlling the critical processing parameters of powder synthesis route. One of the best synthesis methods to produce LSC64 at low processing temperature with good stoichiometry control and preserves homogeneity of the composition along with relatively large surface area after heat treatment is sol-gel method [4,5].

In sol-gel method, chemical agents such as chelant, dispersant and surfactant play an important role on the properties of produced materials. Among the chemical agents, there is lack of study reported on the effects of using surfactant on the properties of the produced cathode materials, particularly LSC64 material. To date, to the best of the authors’ knowledge, there is only one surfactant which is polyethylene glycol (PEG), a non-ionic surfactant has been used in producing the LSC64 material [1,6]. A pure single-perovskite phase of LSC64 was obtained at relatively high calcination temperature ($T_c$) which is 1000 °C. To obtain high purity of LSC64 at a lower $T_c$, the use of other non-ionic surfactants which are polyoxyethylene (10) oleyl ether (Brij-97), polyoxyethylene octyl phenyl ether (Triton-X-100) and polyoxyethylene (20) sorbitan monoooleate (Tween-80) is suggested in the present work. Surfactant has unique ability to enhance compatibility of different particles with different characteristics in a solution, provide favorable site for the growth of particle formation process and reduce temperature required for the single phase formation [7–9]. Thus, this work determines the effects of the different non-ionic surfactants on thermal decomposition, phase formation and microstructure of the LSC64 material prepared through sol-gel method.

2. Experimental procedure

2.1. Synthesis of powder
The details for the synthesis of LSC64 powder material through sol-gel method were described elsewhere [10,11]. A stoichiometric amount of metal nitrate salts of lanthanum (La), strontium (Sr) and cobalt (Co) was first dissolved in deionized water and followed by adding a stoichiometric amount of citric acid and ethylenediaminetetraacetic acid (EDTA). After all the chemicals in the mixture were completely dissolve, the pH of the mixture was adjusted to 0.5. The respective surfactant (Brij-97, Triton-X-100 and Tween-80) was separately added into the mixture and the mixture was stirred for another hour. Then, the mixture was slowly heated at 100 °C − 250 °C and 250 °C − 320 °C to evaporate the water/form a viscous gel and dry the obtained viscous gel, respectively. The produced sponge-like black ash was ground and subsequently was calcined at a $T_c$ in the range of 900 °C to 1100 °C for 5 hours. The as-synthesized and calcined powders prepared using Brij-97, Triton-X-100 and Tween-80 were denoted as S1, S2 and S3, respectively.

2.2. Characterization of powder
Thermal decomposition behavior of the as-synthesized powder and phase formation of the calcined powder were analyzed on a thermogravimetric analysis instrument (TGA, Pyris Diamond TG/DTG analyzer, USA) and an X-ray diffractometer (XRD, D8-Advance, Bruker, Germany), respectively. Microstructure image of the calcined powder was captured using a scanning electron microscope (SEM, Zeiss, Germany).

3. Results and discussion

3.1. Thermal decomposition analysis
Figure 1 depicts the thermogravimetric (TG) curves of the as-synthesized powder of LSC64 prepared using different surfactant with three stages of weight loss. The percentage of weight loss at each stage for each powder is tabulated in Table 1. Weight loss recorded at stage 1 corresponds to the dehydration of water or adsorbed moisture, decomposition of remaining low boiling organic compound and elimination of remaining nitrate species [4,12]. A major weight loss at stage 2 is caused
by the decomposition of residual organic and nitrate compounds and a minor weight loss at stage 3 due to the decomposition of trapped carbonaceous residue [10,13]. The TG curve became a plateau after stage 3 with no further weigh loss indicates that the desired oxide material of LSC64 may form in this region. The results are in line with the results of the previous works reported by Tao et al. [1] and Doorn et al. [14] for the LSC64 and La0.7Sr0.3CoO3-δ materials which were also synthesized through citric acid-ETDA sol-gel method. Based on the TGA results, the as-synthesized powders of S1, S2 and S3 were suggested to be calcined at Tc of 1000 °C, 900 °C and 1100 °C, respectively.

The discrepancy in the percentage of total weight loss for each powder is corresponded to the molecular weight (Mw) of each surfactant and drying temperature (Tdry) of the viscous gel to obtain sponge-like black ash. Tdry increases as Mw of the surfactant increased, and increasing of Tdry reduces the percentage of total weight loss as some of the organic or unrequired compounds were decomposed or eliminated during the drying process. Consequently, the powder dried at higher temperature recorded the lowest percentage of total weight loss during TGA measurement. The explanation is summarized in Table 2.

![Figure 1. TG curve for each as-synthesized powder of LSC64 prepared using different surfactant](image)

**Table 1.** Percentage of weight loss at each stage for each as-synthesized powder of LSC64 prepared using different surfactant

| As-synthesized powder | Stage | Temperature range (°C) | Weight loss (%) | Total weight loss (%) |
|-----------------------|-------|------------------------|-----------------|----------------------|
| S1 (Brij-97)          | 1     | 30 – 130               | 1.22            | 20.98                |
|                       | 2     | 130 – 860              | 19.41           |                      |
|                       | 3     | 860 – 1000             | 0.35            |                      |
| S2 (Triton-X-100)     | 1     | 30 – 170               | 2.52            | 64.26                |
|                       | 2     | 170 – 670              | 59.64           |                      |
|                       | 3     | 670 – 870              | 2.10            |                      |
| S3 (Tween-80)         | 1     | 30 – 160               | 0.82            | 16.99                |
|                       | 2     | 160 – 880              | 14.85           |                      |
|                       | 3     | 880 – 1100             | 1.32            |                      |

**Table 2.** Relationship between molecular weight (Mw), drying temperature (Tdry) and total weight loss

| Surfactant  | Mw (g mol⁻¹) | Tdry (°C) | Total weight loss (%) |
|-------------|--------------|-----------|-----------------------|
|             |              |           |                       |
3.2. Phase formation analysis

The XRD patterns for the calcined S1, S2 and S3 powders are shown in Figure 2. The XRD measurement confirmed the presence of the LSC64 perovskite phase in all powders. All of the perovskite peaks of the LSC64 were matched with the International Centre for Diffraction Data (ICDD) 00-048-0121 (cubic, Pm-3m). The results are in line and comparable with our previous reported works [10,15] and other reported works in the literature [1,3,16]. Besides that, the presence of secondary phases such as Co$_3$O$_4$ (ICDD 00-042-1467), SrCO$_3$ (ICDD 00-005-0418) and La$_2$O$_3$ (ICDD 00-005-0602) are also detected in the XRD patterns. The presence of the secondary phases indicates that the calcined powders of S1, S2 and S3 did not fully crystallized to form a single perovskite phase of LSC64. However, the calcined powders are considered as pure enough as the percentage of the perovskite phase in the calcined powders is more than 90 % (S1 = 92.82 %, S2 = 91.83 % and S3 = 95.22 %). Purity of the synthesized powders should be higher than 90 % for lab-scale powder production. Achieving 100 % purity for lab scale powder synthesis is difficult [13,17]. To achieve higher purity, all of the calcined powders (S1, S2 and S3) are suggested to be calcined at a higher $T_c$ as high purity is very important during electrochemical performance testing for solid oxide fuel cell (SOFC) application as reported in our previous work [18]. Otherwise, other processing parameters such as surfactant concentration, molar ratio of surfactant to metal cation and pH of the solution mixture need to be optimized and controlled in order to produce high purity of LSC64 powder at a lower $T_c$ than 1100 °C. All of these parameters significantly affect the properties and reaction mechanism of surfactant such as wettability to reduce or increase surface tension in solution mixture and micelle formation [19–21].

| Surfactant          | S1  | S2  | S3  |
|---------------------|-----|-----|-----|
| Triton-X-100 (S2)   | 646 | 280 | 64.26 |
| Brij-97 (S1)        | 709 | 300 | 20.98 |
| Tween-80 (S3)       | 1310| 320 | 14.75 |

Figure 2. XRD patterns of the calcined powders of S1, S2 and S3 prepared using different surfactant
3.3. Microstructure analysis
Morphology of the calcined powders prepared using different surfactant is shown in Figure 3. The powders are made up of homogeneous and almost identical particles with regular shape. The particles are dispersed and connected with each other. However, the connection between the particles is different. The Brij-97 (S1) and Tween-80 (S3) based powders have morphology of typical clump-like network structure. The Triton-X-100 (S2) based powder has morphology of flake-like network structure. Besides that, it can be clearly seen the particle size of the calcined powders is also different. S2 ($T_c = 900 \, ^\circ\text{C}$) has smaller particle size than the S1 ($T_c = 1000 \, ^\circ\text{C}$) and S3 ($T_c = 1100 \, ^\circ\text{C}$). The discrepancy is related to the $T_c$ applied to produce each of the powders. Generally, higher the $T_c$, larger the particle size as the particle tend to growth during the heat treatment.

![SEM images of the calcined powders prepared using different surfactant](image)

Figure 3. SEM images of the calcined powders prepared using different surfactant

4. Conclusions
A single perovskite phase of lanthanum strontium cobaltite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$ (LSC64) powder material was successfully prepared through sol-gel method assisted with different non-ionic surfactants namely Brij-97, Triton-X-100 and Tween-80. Thermal decomposition behavior of the as-synthesized powder is affected by the molecular weight of the surfactant and drying temperature of the viscous gel. All of the calcined powder exhibited more than 90% of LSC64 perovskite phase. Additionally, the calcined powder has almost similar powder morphology, but slightly different in the network structure and particle size. Phase purity of the calcined powder is expected to be enhanced by increasing the calcination temperature or controlling the other critical powder processing parameters such as concentration of the surfactant, molar ratio of surfactant to metal cation and pH of the solution mixture. The electrochemical performance of the produced LSC64 powder using different surfactant in this work will be further evaluated for the application SOFC cathode component and the results will be reported elsewhere.

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