Powder Technology 313 (2017) 382–388

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Influence of mixing time on the purity and physical properties of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders produced by solution combustion

Nurul Akidah Baharuddin [a], Andanastuti Muchtar [a,b,*], Mahendra Rao Somalu [a], Mohadeseh Seyednezhad [c]

[a] Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[b] Department of Mechanical and Materials Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[c] Department of Mechanical and Aerospace Engineering, Florida Institute of Technology, Melbourne, FL 32901, USA

ARTICLE INFO

Article history:
Received 6 September 2016
Received in revised form 2 February 2017
Accepted 15 March 2017
Available online 18 March 2017

Keywords:
Solution combustion
Mixing time
Perovskite
Purity
Crystallite size
Particle size

ABSTRACT

This study explored the effects of mixing time on the purity and physical properties of synthesized perovskite ($SrFe_{0.5}Ti_{0.5}O_{3-\delta}$) powders. $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders were prepared with solution combustion, in which various precursor solutions were utilized with different mixing times. The precursor powders were calcined at a certain temperature that was determined via thermogravimetric and Fourier-transform infrared analyses. Each batch of calcined powders underwent X-ray diffraction to analyze the purity and phase formation of the yield. By increasing the mixing time to 45 h, pure cubic-structured $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders were formed and the crystallite size decreased. The average crystallite size decreased from 30.46 to 28.96 nm with the increase of mixing time (from 5 to 45 h). The powders produced after 45 h of mixing exhibited pure phase. These powders were further analyzed using field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS), and energy-dispersive X-ray spectroscopy (EDX). The average particle sizes of 1.5849 and 1.6219 μm were measured with the statistical distribution of micrographs, which were obtained from FESEM, and DLS analysis, respectively. Results obtained from EDX confirmed that the elements were homogenously distributed after 45 h of mixing. To examine the suitability of pure $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders as fuel cell cathode material, electrical conductivity was measured, obtaining a value of 6.32 S cm^{-1}. This value is higher than the electrical conductivity of the same composition of powders synthesized using solid-state method.

1. Introduction

Gas sensors and ceramic electrolyte fuel cells require pure and fine materials. Wet material processing (e.g., sol–gel, dry-freezing, and combustion) offers final products with these desired qualities [1]. Apart from the electrolyte, pure materials at electrodes (anode and cathode) are an important parameter in producing a high-performance ceramic electrolyte fuel cell (also known as solid oxide fuel cell, SOFC) [2,3]. The existence of secondary phase in the electrodes can form the electrical insulating layer, thus affecting the reduction/oxidation reaction rate at the electrodes of SOFC [4]. To produce pure (single-phase) powders for electrodes, wet processing method is suggested rather than solid-state method [5]. The limitations of solid-state synthesis includes the production of large particles and formation of undesired secondary phases [6].

In wet processing method, the high purity of yield is strongly related to its processing parameters, including the starting material composition, fuel/chelating agent selection, and mixing conditions [7–10]. The mixing or stirring condition is considered the simplest parameter, which normally involves manipulation of mixing speed and time. The importance of stirring or mixing has been studied in several processing methods. For wet chemical precipitation, variations in the stirring conditions help to prevent particle agglomeration and produce high homogeneity [11]. The mixing time solves the agglomeration issue; thus, the particle size of materials can be controlled. The porosity of the materials can be monitored; whereas the physical properties directly related to this parameter, such as material strength, can be adjusted [12]. These conditions show the importance of mixing time in controlling the physical properties of materials.

Studies on the production of final materials with high purity confirmed that mixing time (t_m) is a significant parameter influencing yield purity. In hydrothermal and solvothermal processing, t_m plays an important role in eliminating unwanted phases [13,14]. In the sol–gel method, nanosized Al_2O_3 powders are produced after varying t_m from 24 to 48 h [15]. A mixing process was performed before drying for the solution combustion (SC) method. Extensive research on this parameter has not yet been conducted. Most studies related to the combustion method focused on the fuel selection parameter [6,16,17]. In the present study, $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders were prepared by SC under different t_m values. These powders would be used as the cobalt-free cathode of SOFC. The relationship between t_m and the yield purity and properties was investigated.

---

[*] Corresponding author at: Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
E-mail address: muchtar@ukm.edu.my (A. Muchtar).

http://dx.doi.org/10.1016/j.powtec.2017.03.035
0032-5910/© 2017 Elsevier B.V. All rights reserved.

2. Materials and methods

The precursor powders of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ were prepared by SC. All raw materials were purchased from Sigma Aldrich. Metal nitrates, such as strontium nitrate ($Sr(NO_3)_2$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), were dissolved together in deionized water with the as-prepared titanyl nitrate ($TiO(NO_3)_2$). $TiO(NO_3)_2$ was generated from the hydrolysis of titanium butoxide ($Ti(C_4H_9O)_4$) and the nitration of titanium hydroxide, ($TiO(OH)_2$). Glycine (NH_2CH_2COOH) was added to the solution with a known stoichiometric ratio to the nitrates. The glycine/nitrates (G/N) ratio was calculated according to the propellant chemistry principle [18]. The general equation for SC of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ is as follows:

$$\begin{aligned} &Sr(NO_3)_2 + 0.5Fe(NO_3)_3 \cdot 9H_2O + 0.5TiO(NO_3)_2 + xNH_2CH_2COOH \\ &\quad = SrFe_{0.5}Ti_{0.5}O_{3-\delta} + AN_2 + BCO_2 + CH_2O \end{aligned} \tag{1}$$

According to propellant chemistry theory, the sum of oxidizing valence of nitrates is −22.5 and the sum of reducing the valence of glycine is 9. Thus, the elemental stoichiometric coefficient ($\O_e$) was calculated with Eq. (2):

$$\O_e = \Sigma(\text{Oxidizing valence of the nitrate})/-1\Sigma(\text{Reducing valence of the fuel}) \tag{2}$$

From the equation, $\O_e$ is $(-22.5/-9) = 2.5$. The total nitrate molecule is 4.5. Hence, we derived the stoichiometric G/N ratio of $2.5/4.5 = 0.55$.

From the obtained G/N value, x, A, B, and C were calculated on the basis of propellant chemistry theory:

$$\begin{aligned} x &= \O_e \\ &= 2.5 \\ A &= (\text{total nitrate molecule} + x)/2 \\ &= (4.5 + 2.5)/2 \\ &= 3.5 \\ B &= 2x \\ &= 5.0 \\ C &= (5/2)x \\ &= 6.25 \end{aligned}$$

Given the above-mentioned values, the general equation of Eq. (1) becomes:

$$\begin{aligned} &Sr(NO_3)_2 + 0.5Fe(NO_3)_3 \cdot 9H_2O + 0.5TiO(NO_3)_2 \\ &\quad + 2.5NH_2CH_2COOH \\ &\quad = SrFe_{0.5}Ti_{0.5}O_{3-\delta} + 3.5N_2 + 5CO_2 + 6.25H_2O \end{aligned} \tag{3}$$

To determine the calcination temperature, all starting materials were mixed for 1 h before the temperature was increased to 150 °C for drying. After 90 min, the temperature was raised to 350 °C before auto-ignition combustion occurred. The dark precursor powders of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ were produced after the combustion. The precursor powders were subjected to thermogravimetric analysis (TGA) at a static air environment of 30 °C–1200 °C and a heating rate of 10 °C min^{-1} (Pyris Diamond TG/DTG analyzer). Subsequently, Fourier transform infrared (FTIR) analysis was applied to confirm the oxide phase formation (PerkinElmer). The calcination temperature was then derived.

Several batches of starting materials were mixed at different mixing times (t_m = 5, 15, 25, 35, and 45 h). The same step was repeated for drying. The precursor powders obtained after combustion were calcined at 1300 °C for 5 h. Thereafter, each batch of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders produced from different t_m values was studied through X-ray diffraction (XRD). XRD was conducted at room temperature at a range of 10° to 100°; the average crystallite sizes were calculated with Scherrer equation. Powders with high purity underwent particle size analysis through field emission electron microscopy (FESEM) (Hitachi SU8010, Japan) and dynamic light scattering (DLS) (Zetasizer Nano ZS; Malvern Instrument, UK). Elemental analysis was performed using energy-dispersive X-ray analysis (EDX) coupled with FESEM.

As the synthesized powders in this work would be used as the cobalt-free cathode of SOFC, the electrical performance of $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ film was examined. The $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powders underwent ball milling and triple-roll-milling to form $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode ink. Samarium-doped ceria (SDC) powders was pressed into 25 mm spherical substrate using uniaxial pressing machine at 10 MPa (Carver, USA). The $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ cathode ink was screen printed on one side of SDC substrate to form cathode film, which is then called as half cell. The half cell was sintered at 1100 °C for 2 h and underwent electrical conductivity analysis using van der Pauw method at temperature of 600 °C–800 °C under air flow rate of 200 ml/min.

3. Results and discussion

3.1. Thermal decomposition behavior of precursor powder

The thermal decomposition of the precursor powder was studied to observe multiple elimination stages of unwanted phase or elements until the desired perovskite oxide was formed. Fig. 1 presents the TGA (black) and DTG (blue) curves of the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ precursor powder. Decomposition started from 100 °C due to the elimination of water from the precursor powder. Decomposition significantly occurred at two temperature ranges, between 400–600 °C and 800–1000 °C. The sharp downward peak of the DTG curve confirmed the critical weight loss recorded in the above-mentioned temperature region. The recorded weight loss for the first temperature region is attributed to nitrate decomposition, whereas that for the second region is caused by the elimination of carbon residues [18,19]. A total weight loss of 13.16% was recorded for the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ precursor powder at 30–1200 °C. The final weight loss was recorded at approximately 1000 °C; no further losses were observed. Thus, the precursor powder calcination was suggested to be at temperatures above 1000 °C. The weight loss caused by the elimination of unwanted compounds and the formation of the oxide phase can also be observed through FTIR. The $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ precursor powder was calcined at a temperature of 1300 °C, followed by FTIR analysis of the calcined powders to confirm powder purity.

Fig. 2 shows the IR spectrum of the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ powder calcined at 1300 °C. The peaks were recorded at frequencies near 3440, 1600, 1400, and 600 cm^{-1}. The peak at 3440 cm^{-1} can be attributed to the O—H functional group (stretching mode) that belonged to water molecules from environmental humidity, whereas the peaks observed at 1600 and 1400 cm^{-1} were caused by the presence of the same functional group in its bending mode [20]. A sharp peak at approximately 600 cm^{-1} was recorded because of the formation of the desired oxide, which was based on the $SrFeO_{3-\delta}$ parent material [21]. No peaks were

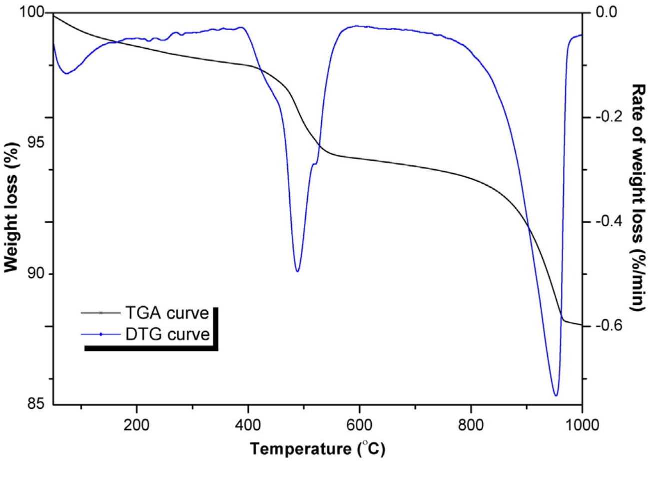

Fig. 1. TGA curve of the $SrFe_{0.5}Ti_{0.5}O_{3-\delta}$ precursor powder.