GLYCINE NITRATE PROCESS FOR THE PREPARATION OF 
(La$_{1-x}$Sr$_x$)$_2$Mn$_{1-y}$Cr$_y$O$_{3.5}$ CATHODE MATERIALS IN SOFC

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In LaMnO$_3$-based cathode materials, A-site cation deficiency increases its thermodynamic stability in SOFC and B-site cation doped with Cr enhances its morphological stability. The present paper reports the preparation of (La$_{1-x}$Sr$_x$)$_2$Mn$_{1-y}$Cr$_y$O$_{3.5}$ by the glycine-nitrate process, which may yield powders of single phase with super-fine particle size. The properties of the ash powders yielded by combustion at three molar ratios of glycine/nitrate were characterized by TEM, DTA, XRD and TG techniques. The mean particle size of the powders after calcination at 650°C for three hours demonstrated all to be less than 1 μm. XRD results showed that for the powder products after calcination at 650°C for three hours a single phase with pseudocubic-type perovskite structure was formed; however, after calcination at 1350°C for half an hour, a single phase with rhombohedral-type perovskite structure was observed.

INTRODUCTION

Perovskite-type Lanthanum manganites, especially with A-site substituted by strontium, are the promising cathode materials for high temperature solid oxide fuel cells (SOFC) due to their high electric conductivity and thermodynamic stability. However, the severe conditions imposed on cathode during SOFC operation at 1000°C arouse many material problems that increase cathode overvoltage and decrease SOFC efficiency to some extent.

Recently, two-phase cathodes consisting of La$_{1-x}$Sr$_x$MnO$_3$ with A-site cation deficiency and yttrium stabilized zirconia (YSZ), which could increase mixed conductivity and improve thermal expansion match between the electrolyte (YSZ) and the cathode, have been considered (1–3). Additionally, low level Cr B-site substituted La$_{1-x}$Sr$_x$MnO$_3$ might decrease oxygen overpotential due to the improvement of morphological stability (4,5).

Moreover, the fabrication of advanced ceramics requires powders of high quality in which the synthesis route plays an important role. In recent years, the glycine-nitrate synthesis method that produces ultrafine powders composed of a single phase containing multi-components has been used to prepare oxide powders such as substituted manganites, chromites and so on (6–8). Advantages over the conventional
amorphous citrate process include rapid and self-sustaining combustion, finer particle size, more homogeneous phase and better crystallized powders.

In this work, \((\text{La}_{1-x}\text{Sr}_x)\text{Mn}_{1-y}\text{Cr}_y\text{O}_{3+\delta}\) (LSMC) is prepared by the glycine-nitrate process (GNP) and the properties of the ash powders are characterized by XRD, DTA/TG and TEM in order to research the process of synthesis and search the best conditions of the synthesis route.

**EXPERIMENTAL**

The glycine-nitrate synthesis of \((\text{La}_{1-x}\text{Sr}_x)\text{Mn}_{1-y}\text{Cr}_y\text{O}_{3+\delta}\) \((0.2 \leq x \leq 0.4, 0.05 \leq y \leq 0.15, 0.90 \leq z \leq 0.98)\) was carried out. Reagent-grade metal nitrates were used. The stock solutions were prepared by dissolving metal nitrates in deionized water. The molar concentrations on the basis of cation of the stock solutions, which included 1M-Sr(NO₃)₂, 1M-Mn(NO₃)₂, 0.5M-La(NO₃)₃ and 0.5M-Cr(NO₃)₂, were determined by EDTA titration. The stock solutions were mixed at an appropriate volume proportion to make a certain compound. NH₄NO₃ was added in the form of standard solution to adjust the stoichiometry between fuel (glycine) and oxidant. After reagent-grade powder-like glycine was added by weight, the solution was stirred in an electromagnetic stirrer for half an hour or more. Then, the solution was transmitted to a 1500ml stainless-steel container covered by a 240-mesh stainless-steel sieve on an electric heater. Finally, combustion occurred at a temperature of 210–230°C, which was measured by a surface-thermometer.

The properties of the ash particles synthesized by this route at three different molar ratios of metal nitrates/glycine were characterized by TEM, DTA/TG and XRD. The X-ray diffraction patterns were taken with an RAX-10 system. The differential thermal analysis was carried out with a CDR-1 differential thermal analyzer and thermogravimetric data was measured with a WRT-2 thermogravimetric balance. The transmission electron micrographs were taken with a JEM-2000CX.

After calcination at 650°C for three hours, powders were prepared. Particle size of the products was investigated by a BI-90 particle sizer. Guinier geometry was used to examine the crystal structure of the products. The X-ray diffraction patterns of the powders calcined at 1350°C for half an hour were taken with the same apparatus as above.

**RESULTS AND DISCUSSION**

In the GNP, the following phenomena were observed. The dark green transparent honey-like precursor was prepared after evaporation of the metal nitrates+ammonium nitrate/glycine/water solution with the same color. Heated to a higher temperature, combustion occurred at the point of autoignition of the precursor. In the present investigation, this point, with respect to \((\text{La}_{0.7}\text{Sr}_{0.3})_{0.94}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_{3.5}\), was...
217–222°C, which was irrespective of the molar ratio of metal nitrates/glycine for the same component when the stoichiometry was adjusted by the addition of NH₄NO₃.

As shown in Fig.1, thermogravimetric measurement and differential thermal analysis (DTA/TG) were carried out on the ashes synthesized by GNP at three different molar ratios of the metal nitrate/glycine with the addition of NH₄NO₃ to adjust the stoichiometry. Fig.1(a), (b) and (c) corresponded to the molar ratios of 1:2, 1:1.5 and 1:1, respectively. In all the three figures, the first three peaks and the correspondent weight losses were the same. The first weight loss and endothermic peak from 60 °C to 130°C represented a loss in water. The second and the third exothermal peaks, which depicted the combustion of the dehydrated organic residues and decarbonization in the ashes, were close to each other so that only one major weight loss was detected around 180–450°C. In Fig.1(a) and (b), there existed an endothermal peak at the temperature of 460–550°C that probably represented the decomposition of crystalline strontium nitrate. By contrast, the same peak was not observed in Fig.1(c). However, all the figures in Fig.1 showed that an obvious weight loss occurred around 500–600°C that was caused by the decomposition of crystalline or amorphous Sr(NO₃)₂. The XRD patterns of the three types of ashes, in Fig.2, revealed that pseudocubic-type perovskite ash particles were prepared, and confirmed the existence of crystalline Sr(NO₃)₂. Nonetheless, only the most intensive diffraction peak of Sr(NO₃)₂ was available in Fig.2(c), which was used to describe the same type of ashes as Fig.1(c).

L. A. Chick, L. P. Pederson, et al.(6) also found the existence of Sr(NO₃)₂ and recommended that adjusting the stoichiometry to the glycine-rich side was necessary to avoid the formation of intermediate nitrate phases in the ash. In the authors’ opinion, the crystallinity of the compound synthesized by GNP method depended on the completeness of combustion, which was determined by the molar ratio of metal nitrates/glycine. According to the thermogravimetric data, when the molar ratios of metal nitrates/glycine are 1:2 and 1:1.5, the relative rates of total weight loss were 14.6% and 21.0%, respectively. Obviously, an excess amount of glycine resulted in less residue and higher crystallinity of Sr(NO₃)₂ although the stoichiometry was adjusted by the addition of NH₄NO₃.

Fig.3, Fig.4 and Fig.5 show the bright-field transmission electron micrographs of the ash particles prepared by GNP at different molar ratios of metal nitrates/glycine corresponding to 1:1, 1:1.5 and 1:2, respectively. Compared to Fig.4 and Fig.5, Fig.3 shows that there existed more remnants containing intervening amorphous phases in the ashes. Meanwhile, the incomplete combustion resulted in a low reaction temperature, which was the reason that the crystallinity of Sr(NO₃)₂ was so low that only the most intensive diffraction peak of Sr(NO₃)₂ was observed in Fig.2(c). In addition, Fig.3 revealed that the ash particles were partially agglomerated and linked together in chains with the mean particle size of ~100nm. By contrast, in Fig.5, the finer ash particles (10–50nm in diameter) were dispersed more homogeneously and
less residue and agglomeration occurred than as shown in Fig. 4 and Fig. 3 due to the more complete combustion. Fig. 4 revealed that the diameter of the ash particles was around 10–50nm, and the properties of the ash particles, with respect to the crystallinity and the amount of residue containing amorphous nitrate phases, ranked second among the three types of ash particles.

In general, the properties of the ash particles prepared by GNP route depended upon the molar ratio of metal nitrates/glycine that had a large influence on the completeness of the combustion.

After the ashes were calcined at 1350°C for one half hour, rhombohedral-type perovskite LSMC of single-phase was detected by XRD patterns (in Fig. 6). Nevertheless, such a high temperature was not necessary for the complete calcination of the ashes. In fact, after being calcined at 650°C for three hours, single-phase LSMC with pseudocubic-type perovskite structure was obtained and examined by Guinier geometry method (shown in Table 1). The mean particle size of the three types of powders was 0.2–0.4μm (shown in Fig. 7).

Table 1. Guinier geometric data for the \((La_{0.7}Sr_{0.3})_{0.94}Mn_{0.9}Cr_{0.1}O_{3.8}\)

|        | 1:2* |       | 1:1.5 |       | 1:1  |       |
|--------|------|-------|-------|-------|------|-------|
| \(2\theta\) | D     | \(2\theta\) | D     | \(2\theta\) | D     | \(2\theta\) | D     |
| 22.863 | 3.8866 | 22.865 | 3.8862 | 22.765 | 3.9030 |
| 32.542 | 2.7493 | 32.604 | 2.7442 | 32.572 | 2.7468 |
| 40.167 | 2.2432 | 40.195 | 2.2417 | 40.152 | 2.2442 |
| 46.782 | 1.9403 | 46.813 | 1.9391 | 46.832 | 1.9383 |
| 52.779 | 1.7331 | 52.758 | 1.7337 | -------- | -------- |
| 58.113 | 1.5860 | 58.211 | 1.5836 | 58.130 | 1.5860 |

*: Sample No. corresponding to the molar ratio of metal nitrates/glycine.

A. Chakraborty, P. S. Devi and H. S. Maiti (9) reported that strontium substituted lanthanum manganites were formed by the autoignition of carboxylate-nitrate gels (ACNG). In their work, the ashes prepared by ACNG route consisted of the impure phase of SrCO₃ and the average particle size of \(La_{0.7}Sr_{0.3}MnO₃\) calcined at the complete firing temperature of 850°C for 6 hours was ~1.61μm. By contrast, in our work, \((La_{0.7}Sr_{0.3})_{0.94}Mn_{0.9}Cr_{0.1}O_{3.8}\) ashes prepared by GNP contained the intermediate nitrate phase of Sr(NO₃)₂ and the mean particle size of the powders calcined at 650°C for 3 hours was 0.2–0.4 μm.

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CONCLUSIONS

The preparation of powders of LSMC of high quality by GNP was very simple and convenient. The properties of the ash particles depended upon the molar ratio of metal nitrates/glycine when the stoichiometry was adjusted by the addition of NH$_4$NO$_3$. Adjusting the molar ratio to glycine-rich side is beneficial to the preparation of ash particles of high quality. The mean advantages of GNP over autoignition of carboxylate-nitrate process include finer particle size, better crystallinity and lower complete calcination temperature.

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Weight loss, %

Figure 1. DTA/TG data for the (La0.75Sr0.25)0.94Mn0.95Cr0.05O3.8 ashes up to 700°C, which were prepared by GNP at the molar ratios of the metal nitrates/glycine corresponding to (a) 1:2, (b) 1:1.5, (c) 1:1.
Figure 2. X-ray diffraction patterns for the (La$_{0.7}$Sr$_{0.3}$)$_{0.94}$Mn$_{0.9}$Cr$_{0.1}$O$_{3.8}$ ashes, which were prepared by GNP at the molar ratios of the metal nitrates/glycine corresponding to (a) 1:2, (b) 1:1.5, (c) 1:1.

Figure 3. The transmission electron micrograph for the (La$_{0.7}$Sr$_{0.3}$)$_{0.94}$Mn$_{0.9}$Cr$_{0.1}$O$_{3.8}$ ashes, which were prepared by GNP at the molar ratio of the metal nitrates/glycine corresponding to 1:1.
Figure 4. The photograph of TEM for the \((\text{La}_{0.7}\text{Sr}_{0.3})\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_{2.5}\) ashes, which were prepared by GNP at the molar ratio of the metal nitrates/glycine corresponding to 1:1.5.

Figure 5. The photograph of TEM for the \((\text{La}_{0.7}\text{Sr}_{0.3})\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_{2.5}\) ashes, which were prepared by GNP at the molar ratios of the metal nitrates/glycine corresponding to 1:2.
Figure 6. X-ray diffraction pattern for the (La$_{0.7}$Sr$_{0.3}$)$_{0.96}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ powders, which were prepared by calcining the ashes at 1350°C for half an hour.

Figure 7. The particle size distribution curves of the (La$_{0.7}$Sr$_{0.3}$)$_{0.96}$Mn$_{0.9}$Cr$_{0.1}$O$_{3-\delta}$ powders, which were prepared by calcining the ashes at 650°C for 3 hours corresponding to the molar ratios of the metal nitrates/glycine of (a) 1:2, (b) 1:1.5, (c) 1:1.