Investigation of precursors in the preparation of nanostructured La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ via a modified combined complexing method

Jing Shao, Youkun Tao, Jianxin Wang, Cheng Xu, Wei Guo Wang*

Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 519 Zhuangshi Ave., Ningbo, Zhejiang 315201, PR China

**A R T I C L E   I N F O**

Article history:
Received 11 March 2009
Received in revised form 10 April 2009
Accepted 16 April 2009
Available online 23 April 2009

Keywords:
Electrode materials
Nanostructures
Chemical synthesis
Sol–gel synthesis

**A B S T R A C T**

A complexing precursor of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ was synthesized through a modified combined complexing method to prepare homogenous La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ nanopowders with high yield at very low pH values. Precursors of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ compound with single chelator and of individual La, Sr, Co, Fe cations with combined chelators were also prepared and characterized. Fourier transform infrared spectroscopy results indicated EDTA could incorporate the Co, Fe cations into soluble complex under pH < 1. Using the citric acid–EDTA in this process could ensure the complexation of all cations and the best molar ratio of EDTA to metal cations was 0.5:1. Calcination of the combined complex precursor, according to XRD patterns, resulted in the crystallization of single phase LSCF by 700 °C. FESEM and BET analysis showed the calcined powder was homogenous and consisted of particles having sizes of approximately 70 nm. It is found that the sample of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ sintered at 1200 °C has a higher conductivity than at 1100 °C or 1300 °C, and the highest conductivity reaches 284.5 S cm$^{-1}$ at 700 °C.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Perovskite-type oxide (La,Sr)(Co,Fe)O$_3$ (LSCF), a good mixed electronic and ionic conductor (MIEC), is one of the most promising candidates for intermediate temperature solid oxide fuel cells (IT-SOFC) cathodes [1–4]. LSCF offers higher conductivity with increasing Sr content. On the other hand, thermal expansion coefficient (TEC) is reduced to a value close to that of YSZ or CGO as the Fe content increases [5,6]. As a compromise between conductivity, catalytic activity and TEC, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ is the most common chemical composition for the cathode applications of IT-SOFC [7–9].

LSCF and related perovskites have been synthesized by numerous methods [10–16]. Among them, the Pechini method has attracted extensive attention [10–13]. Pechini method has the advantage that the stoichiometry and purity can be controlled precisely by the formation of a gelled complex precursor of metals, chelating agents such as citric acid or EDTA and a polyalcohol. Pyrolysis of the precursor creates an end product of high purity, homogeneous morphology and ultrafine particle size [13].

In this study, a modified combined complexing method was used for the preparation of the La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ compound. This combined complexing method was reported for preparing series of perovskite oxides, with citric acid and EDTA as the combined chelating agents [17,18]. The combined chelating agents tend to form stable complexes of a wide range of metals which are more insensitive to pH value than a single one in the Pechini method. However, it is previously reported that a considerable amount of NH$_3$ solution had to be added in order to dissolve EDTA and adjust the pH value of the precursor solution up to 2.8 (usually 7.0 in the Pechini method) [18]. As nitrates are usually used in the synthesis of perovskite oxides, there will be a lot of NH$_4$NO$_3$ in the precursor solution. This produces a large volume of gas during pre-heat treatment which inflates the precursor to overexpand the container seriously, resulting in a poor yield. In order to obtain products of both high yield and high quality, this procedure is modified in this study by optimizing the amount of the combined chelating agents as well as sparing the addition of NH$_3$ solution. Agglomerate-free, homogeneous nanopowders of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ were prepared with a yield of 99% via the modified combined complexing procedure. Different from the traditional one, the pH value of the precursor solution is under 1.0 and no NH$_3$ solution was needed in the modified process. Consequently the volume of LSCF gel can be avoided swelling out seriously. A high yield of LSCF product is thus guaranteed and the procedure becomes simpler.

A systematic study will be presented in this report on the synthesis and characterization of the combined complex precursor of the La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ Compound. For comparison, precursors of the individual La, Sr, Co, Fe cations and of the LSCF compound with a single chelating agent were investigated to obtain further insight into the molecular constitution of the precursors.

* Corresponding author. Tel.: +86 574 8791 1363; fax: +86 574 8668 5139. E-mail address: wgwang@nimte.ac.cn (W.G. Wang).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.04.075
2. Experimental

2.1. Materials

All reactants were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, and used as received. Starting materials consisted of lanthanum(III) oxide (La2O3; 4N), strontium nitrate (Sr(NO3)2; 99.5%), cobalt(II) nitrate hexahydrate (Co(NO3)2·6H2O; 95%), iron(III) nitrate nonahydrate (Fe(NO3)3·9H2O; 98.5%), citric acid (99.5%), ethylenediamine tetraacetic acid (99.5%) and 67 wt% nitric acid (analytical grade).

2.2. Synthesis

Precursors were prepared by dissolving the stoichiometric amount of metal nitrates (lanthanum nitrate was prepared by dissolution of La2O3 in a nitric acid solution) in deionized water at room temperature followed by vigorous stirring. Subsequently, citric acid (CA) and EDTA were added under heating and stirring over several hours. Seven precursors were investigated: La0.6Sr0.4Co0.2Fe0.8O3·9H2O (with CA–EDTA combined chelators), La0.6Sr0.4Co0.2Fe0.8O3·9H2O with CA chelator, La0.6Sr0.4Co0.2Fe0.8O3·9H2O with EDTA chelator, individual La3+, Sr2+, Co2+, Fe3+ with CA–EDTA combined chelators. The seven precursors will be referred as LSCF–CA precursor, LSCF–CE precursor, LSCF–CA–EDTA combined chelators, LSCF–CA–EDTA combined chelators, LSCF–CE precursor, La–CE, Sr–CE, Co–CE, Fe–CE precursor, respectively. In a typical synthesis of LSCF–CE precursor, La2O3 (4.8871 g, 0.03 mol) was dissolved into 10 mL deionized water while 6 mL 67 wt% nitric acid solution was heated and stirred at 75°C until it gelled. The molar ratio of metal:CA–EDTA was 1:1.5:0.5. The combined complex precursor was pre-heated at 120°C for 10 h followed by calcination at 700°C for 5 h to give black LSCF powder. A yield of 95% was obtained.

2.3. Characterization

All precursors and a sample of CA–EDTA mixture without any metallic ion, hereafter called bare sample, were dried at 60°C before characterization. The precursors and bare sample were characterized by a Fourier transform infrared spectroscopy (Nicolet 6700), in the range of 400–4000 cm⁻¹. The electronic conductivity as a function of temperature for resultant LSCF powders was measured using four-probe DC measurement. The LSCF powders were first milled and mixed with 8 wt% poly(vinyl butyral-co-vinyl alcohol-co-vinyl) acetate (PVB; Sinopharm Chemical Reagent Co. Ltd.) binder, then pressed into rectangular-shaped pellets at 300 MPa and sintered in air at 1200°C, 1200°C, 1300°C for 5 h, respectively.

3. Results and discussion

3.1. Precursor investigation

Table 1 summarizes the molar ratio of metal:CA–EDTA and eye-inspection results for different precursor solutions during the synthesis. The variation of the appearances of the precursors was related with the reaction between the chelating agents and metal ions. In preparing the bare sample, white precipitation of EDTA existed in the citric acid solution all along because of the low solubility of EDTA in acidic solution. While for LSCF–EDTA and LSCF–CE precursor, a proper amount of EDTA could be dissolved quickly in the metal nitrate solutions under heating. No NH3 solution was ever used and the pH value maintained less than 1.0. Further investigations found that the maximum molar ratio of EDTA to total metallic ions was up to 0.5:1 to ensure these results. Related with the color change of the two precursors, it seemed that the dissolution of EDTA in these acidic solutions could be promoted by its reaction with metal ions.

Fig. 1. FIIR spectra of the individual chelating agents and the bare sample.

Fig. 2. FIIR spectra of LSCF complex precursors formed by different chelators.
correspond to H₂O and asymmetric NO₃⁻ vibration, respectively [21]. In the spectra of the LSCF–CA complex precursor, C=O stretching vibration appears at 1720 cm⁻¹. The carbonyl absorption is shifted to lower frequency with respect to CA in Fig. 1, which indicates a change in the vibration status of CA upon coordination to the metal ions [22–24]. New vibration at 1590 cm⁻¹, which is due to the stretching mode for carboxylate ions of metal citrate, can be clearly seen. It suggests the presence of excess CA and unbound metal cations. It is thus indicated that an individual chelating agent of CA cannot bind all the metal cations in this process.

In the spectra of the LSCF–EDTA complex precursor, the vibration at 1635 cm⁻¹ is related to the C=O stretching mode for the chelated carboxylic groups of EDTA, which is also shifted to lower frequencies [25]. By comparison with the result of previous experimental observations, it can be concluded that a considerable amount of EDTA could be dissolved in an acidic solution of LSCF precursor directly by coordinating the metal cations into a soluble form.

The FIIR spectrum of the LSCF–CE complex precursor has both the vibrations due to C=O stretching mode of chelated CA (~1740 cm⁻¹) and EDTA (~1620 cm⁻¹). The molar ratio of CA:EDTA:metal was 1.5:0.5:1, which was found to be the most appropriate ratio through series experiments. The pH value of precursor solution was maintained less than 1.0. It is worth noting that in this case, any vibration associated with metal citrate ions has not been detected. This indicates the combined chelating agents, CA with EDTA, can eliminate the occurrence of unbound metal cations so as to ensue the complexation of all metal cations to give homogenous precursors. In addition, no precipitation has been observed through the gelation process, indicated this complex precursor is also stable.

Table 1
Summary of the molar ratios (M = metal ions, CA = citric acid) and eye-inspection results for different precursor solutions during the synthesis.

<table>
<thead>
<tr>
<th>Precursor solution</th>
<th>[M]:[CA]:[EDTA]</th>
<th>Color</th>
<th>Precipitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare sample</td>
<td>0:1.5:0.5</td>
<td>Achromatous</td>
<td>White precipitation</td>
</tr>
<tr>
<td>LSCF–CA</td>
<td>1:1.5:0.5</td>
<td>Orange to brown</td>
<td>Clear solution</td>
</tr>
<tr>
<td>LSCF–EDTA</td>
<td>1:0:0.5</td>
<td>Orange to wine</td>
<td>Clear solution</td>
</tr>
<tr>
<td>LSCF–CE</td>
<td>1:1.5:0.5</td>
<td>Orange to wine</td>
<td>Clear solution</td>
</tr>
<tr>
<td>La–CE</td>
<td>1:1.5:0.5</td>
<td>Achromatous</td>
<td>White precipitation</td>
</tr>
<tr>
<td>Sr–CE</td>
<td>1:1.5:0.5</td>
<td>Achromatous</td>
<td>White precipitation</td>
</tr>
<tr>
<td>Co–CE</td>
<td>1:1.5:0.5</td>
<td>Red to wine</td>
<td>Clear solution</td>
</tr>
<tr>
<td>Fe–CE</td>
<td>1:1.5:0.5</td>
<td>Brown to nut-brown</td>
<td>Clear solution</td>
</tr>
</tbody>
</table>

* a Before the chelating agent (CA or EDTA or CA and EDTA) was added in the metal nitrate solution.
* b After the chelating agent (CA or EDTA or CA and EDTA) was added in the metal nitrate solution.
* c After EDTA was added in the precursor solution.

To obtain better insight into the chelating process of the combined complex precursor, the individual La, Sr, Co, Fe precursors were investigated (see Table 1). The solubility of EDTA varies in each precursor solution, reflecting the different reactivity of each species. For Fe precursor, EDTA was dissolved completely in 10 min. For Co precursor, the time for complete dissolution is about 20 min, whereas for La precursor it took 4 h to dissolve all EDTA and a large number of precipitation occurred during further heating. For Sr precursor, it seems that EDTA could hardly be dissolved in the solution. These indicate, in this condition, EDTA is able to form very stable complexes with Fe, Co cations and an unstable complex with La cation, but cannot form complex with Sr cation basically.

Fig. 3 shows FIIR spectra of the individual metal complex precursors formed by CA–EDTA chelators. In the spectrum of Fe and Co precursors, main vibrations are due to the following: H₂O (~3430 cm⁻¹, 3420 cm⁻¹), C=O stretching of chelated CA (~1730 cm⁻¹), C=O stretching of chelated EDTA (~1620 cm⁻¹), NO₃⁻ vibration or C–O stretching (~1385 cm⁻¹), C–O stretching (~1190 cm⁻¹). Spectra of these two precursors show infrared bands similar to those observed in the LSCF–CE spectra, demonstrating Fe, Co cations can be bound completely by CA–EDTA chelators. In the Sr precursor spectra, the chelated EDTA related vibration cannot be observed. However, vibrations at 3010 cm⁻¹, which are characteristics of free EDTA, can be clearly seen. The corresponding band related to C=O vibration (~1690 cm⁻¹) of free EDTA may overlap with that at 1700 cm⁻¹, which is due to C=O vibration of chelated CA. These observations show Sr cation hardly reacts with EDTA and is coordinated by CA alone. In the spectrum of the La precursor, main vibrations are due to H₂O (~3430 cm⁻¹), C=O stretching of chelated CA (~1730 cm⁻¹), C=O stretching of lanthanum carboxylate (~1600 cm⁻¹), NO₃⁻ vibration or C–O stretching (~1385 cm⁻¹). These infrared bands indicate La cation can form complex with CA but not with EDTA.

On the whole, CA can form complex with any species of La, Sr, Co, Fe cations in this process, but cannot totally coordinate all of them. EDTA can form stable complex only with Co and Fe cations. The combined CA–EDTA can bind all the four metal cations completely. Furthermore, EDTA forms complex with most metal cations at the molar ratio of 1:1, so that the maximum ratio as well as the best ratio of EDTA to metal cations in this case should be equal to that of Co and Fe cations to the total metal cations, which is 0.5:1 for La₀.₅Sr₀.₅Co₀.₂Fe₀.₈O₃–δ compound. This is consistent with experimental results.

Another important observation that should be noted is that the infrared spectrum of the LSCF combined complex precursor (Fig. 2) cannot be interpreted as a pure superposition of the individual La, Sr, Co, Fe precursors infrared spectrums. This, accordingly, indicates the La, Sr, Co, Fe cations have strong interaction during chelation. Similar observations have been reported in the synthesis of BaTiO₃ [26] and La₂Mo₂O₉ [27] using polymeric precursor method.
Fig. 4. X-ray diffraction patterns of the LSCF-CE combined complex precursor after pyrolysis (250 °C) and calcinations at 600 °C or 700 °C.

3.2. Properties of LSCF powders

The XRD patterns of the LSCF-CE combined complex precursor pyrolyzed at 250 °C and further calcined at 600 °C or 700 °C are shown in Fig. 4. It can be seen that the pyrolyzed precursor consists of amorphous materials, while calcined powders had well-crystallized perovskite structure of LSCF. Although a small amount of SrCO3 phase could be observed in the pattern of powders calcined at 600 °C, the impurity phase totally disappeared and a single perovskite phase was formed completely when the sintering temperature reaches 700 °C.

Fig. 5 shows the morphologies of powder particles of the LSCF-CE combined complex precursor after calcined at 700 °C. The low magnification micrograph, shown in Fig. 5a, demonstrates a homogeneous morphology with a narrow size distribution and hard agglomerate-free nature of the calcined powders. The high magnification micrograph in Fig. 5b highlights the particulate morphology of the calcined LSCF. The particles are basically spherical in shape and the particle diameters are approximately 70 nm.

Similar morphologies and pure perovskite phases were obtained as the product scale was enlarged from 2 g per run to 100 g per run. The yield of LSCF powders in all cases was very close to the theoretical one. This combined complex method for preparing LSCF was thus highly reproducible and effective.

The BET surface area for the precursor calcined at 700 °C for 5 h was 14.65 m²/g. Using the surface area and assuming all particles are spherical, the average particle size (d_BET) can be calculated for the powder using:

\[
d_{\text{BET}} = \frac{6}{\rho S_v}
\]

where ρ is the materials density and S_v the surface area of the sample. Using the density determined from XRD analysis of calcined LSCF powder (6.36 g cm⁻³), the calculated d_BET for the precursor was 64 nm. This is in good agreement with the observed particle size from FESEM, suggesting the majority of particles are nanostructured.

The effect of sintering temperature on the electronic conductivity was investigated by four-probe DC measurement. The La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋ₓ powders synthesized from precursor with EDTA:metal ions molar ratio of 0.5:1 were pressed into pellets. The pellets, which were labeled Sample 1, Sample 2 and Sample 3, were sintered at 1100 °C, 1200 °C, 1300 °C for 5 h, respectively. Fig. 6 shows log(σT) as a function of 10³/T from 20 °C to 1000 °C for the three LSCF samples. The measured electrical conductivity for each sample increased with increasing temperature, reached a maximum value at a characteristic temperature and then decreased with increasing temperature. As can be seen in Fig. 6, all the curves maintained linear at low temperature but started to bend downward at some particular high temperatures. Similar results have been reported in previous literatures [5,28]. Tai et al. [5] found that the increase in electrical conductivity with increasing temperature for LSCF is due to the small polaron conduction, while the decline of conductivity may result from the ionic compensation of oxygen vacancy. The maximums of electronic conductivity dependence on temperature for Sample 1, Sample 2 and Sample 3 were 2145 S cm⁻¹ at 500 °C, 2845 S cm⁻¹ at 700 °C and 276 S cm⁻¹ at 700 °C.
respectively. The relative densities of sintered pellets were 83%, 92% and 93% of theoretical one for Sample 1, Sample 2 and Sample 3, respectively. Sample 2, which was sintered at 1200 °C, exhibited the highest conductivity. The lowest conductivity for Sample 1 is understandable because conductivity is known to decrease with increasing porosity [29]. However, the maximum of electronic conductivity for Sample 3 decreased slightly as the density increased compared with Sample 2. This might be attributed to the serious loss of cobalt by diffusion at such high temperature.

4. Conclusions

Homogenous nanopowders resulting from the calcinations of a combined complex precursor of the La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3}$−$\delta$ compound were successfully prepared via the modified combined complexing method. Results of the FIIR analysis demonstrated a proper amount of EDTA can be directly dissolved in the acidic solution by forming solvable complex compound with metal cations, thus no NH$_3$ solution was needed. So the loss of product was avoided and the procedure was simplified. In this case, the combined CA–EDTA chelator is able to bind the metal cations in the precursor solution completely. Calcination of the precursor gave rise to ultrafine LSCF powders of pure perovskite phase and uniform morphology. The modified combined complex method proved to be a simple and effective route for the preparation of LSCF compound.

Acknowledgements

This work was supported partly by the National High Technology Research and Development Program of China (863 Program, Grant No. 2007AA05Z140) and Qian Jiang Program (Grant No. 0805011016).

References