



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

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ARTICLE INFO

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

ABSTRACT

A complexing precursor of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ was synthesized through a modified combined complexing method to prepare homogenous $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ nanopowders with high yield at very low pH values. Precursors of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 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 $\text{pH} < 1$. 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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ sintered at 1200°C has a higher conductivity than at 1100°C or 1300°C , and the highest conductivity reaches 284 S cm^{-1} at 700°C .

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1. Introduction

Perovskite-type oxide $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (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, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 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_4NO_3 in the precursor solution. This produces a large volume of gas during pre-heat treatment which inflates the precursor to overflow 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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 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 chelation of the combined complex precursor of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ 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.

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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 (La_2O_3 ; 4N), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$; 99.5%), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 99%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 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 La_2O_3 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: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with CA–EDTA combined chelators, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with CA chelator, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with EDTA chelator, individual La^{3+} , Sr^{2+} , Co^{2+} , Fe^{3+} with CA–EDTA combined chelators. The seven precursors will be referred as LSCF–CE precursor, LSCF–CA precursor, LSCF–EDTA precursor, La–CE, Sr–CE, Co–CE, Fe–CE precursor, respectively. In a typical synthesis of LSCF–CE precursor, La_2O_3 (4.8871 g, 0.03 mol) was dissolved into 10 mL deionized water while 6 mL 67 wt% nitrite acid was dropped in under the condition of stirring to form a clear lanthanum nitrate solution. Then $\text{Sr}(\text{NO}_3)_2$ (4.2327 g, 0.02 mol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.9103 g, 0.01 mol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (16.16 g, 0.04 mol) and 100 mL deionized water were added into this solution. After complete dissolution of the salts, CA (31.521 g, 0.15 mol) and EDTA (14.622 g, 0.5 mol) were added into the mixed solution without any NH_3 solution. The resultant 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 99% 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 X-ray diffraction patterns of the LSCF powder obtained from the combined complex precursor were collected using a diffractometer (D8 Advance, Bruker) operating at 40 kV and 40 mA with $\text{Cu K}\alpha$ radiation source. X-ray detections were conducted at a sampling interval of 0.05° and 10 s dwell time in the 20–80° 2θ range. The LSCF particle morphologies were observed by field emission scanning electron microscopy (FESEM) (S-4800, Hitachi).

Surface area analysis of the derived powder was performed by nitrogen absorption at 77 K using an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp.). Prior to analysis, the samples were outgassed at 200 °C under vacuum for 24 h. The specific surface area was calculated using BET theory.

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 1100 °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 NH_3 solution was ever used and the pH value maintained less than 1.0. Further investigation found that the maximum molar ratio of EDTA to total metallic ions was up to 0.5:1 to ensue 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.

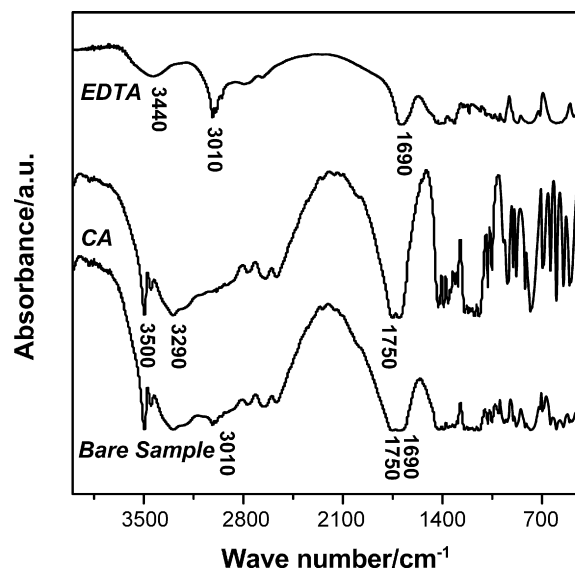


Fig. 1. FTIR spectra of the individual chelating agents and the bare sample.

Fig. 1 shows FTIR spectra of the individual chelating agents and the bare sample. Spectra of EDTA and CA correlate with literature data [19,20]. In the spectrum of EDTA, a broadened absorption band at 3430 cm^{-1} is observed to be associated with molecular water. The sharp absorption band at 3010 cm^{-1} is related to the diametric O–H stretching of intermolecular carboxylic acid. The strong vibration at 1690 cm^{-1} corresponds to asymmetric C=O stretching, and the corresponding symmetric C=O stretching appears at 1440 cm^{-1} . In the spectrum of CA, the bands at 3500 cm^{-1} and 3290 cm^{-1} can be attributed to a single bridge OH vibration and the O–H vibration of intermolecular hydrogen bonds. Asymmetric C=O stretching vibration appear at about 1750 cm^{-1} , whereas the symmetric ones appear at $\sim 1430 \text{ cm}^{-1}$. In the spectrum of the bare sample, no new vibration has been detected, which is absent in the spectrum of CA or EDTA. Furthermore, it has been observed that the spectrum of the bare sample is a simple superposition of the individual chemical CA and EDTA. This could indicate that no polymerization reaction occurs between CA and EDTA.

The FTIR spectra for LSCF–CA, LSCF–EDTA and LSCF–CE precursor are shown in Fig. 2. The bands at about 3420 cm^{-1} and 1380 cm^{-1}

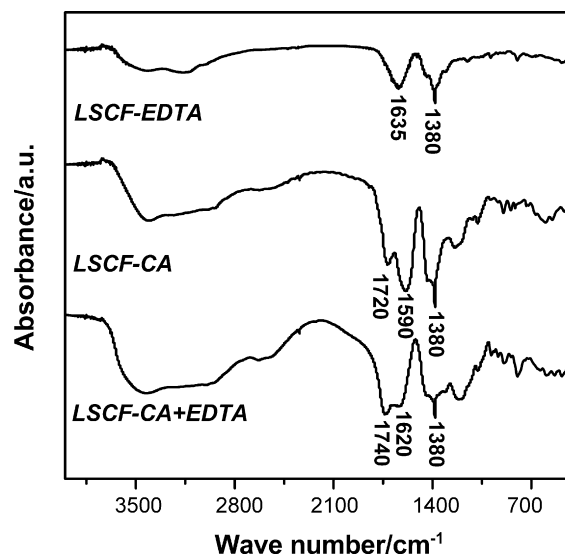


Fig. 2. FTIR spectra of LSCF complex precursors formed by different chelators.

Table 1

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

Precursor solution	[M]:[CA]:[EDTA]	Color	Precipitations
Bare sample	0:1.5:0.5	Achromatous	White precipitation ^c
LSCF-CA	1:1.5:0	Orange ^a to brown ^b	Clear solution
LSCF-EDTA	1:0:0.5	Orange ^a to wine ^b	Clear solution
LSCF-CE	1:1.5:0.5	Orange ^a to wine ^b	Clear solution
La-CE	1:1.5:0.5	Achromatous	White precipitation ^c
Sr-CE	1:1.5:0.5	Achromatous	White precipitation ^c
Co-CE	1:1.5:0.5	Red ^a to wine ^b	Clear solution
Fe-CE	1:1.5:0.5	Brown ^a to nut-brown ^b	Clear solution

^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.

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 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 ensure 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.

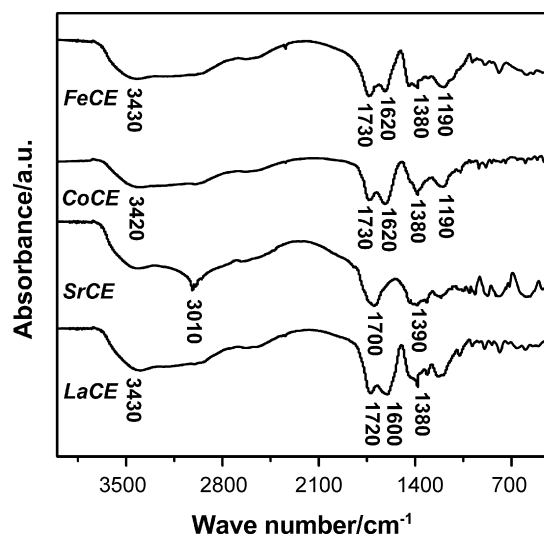
To obtain better insight into the chelating process of the combined complex precursor, the individual La, Sr, Co, Fe precursors were investigated (see Table 1). The solubility of EDTA varies in each precursor solution, reflecting the different reactivity of each species. For Fe precursor, EDTA was dissolved 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.

This conclusion is also confirmed by the results of FIIR analysis. 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 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-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. 3.** FIIR spectra of individual metal combined complex precursors.

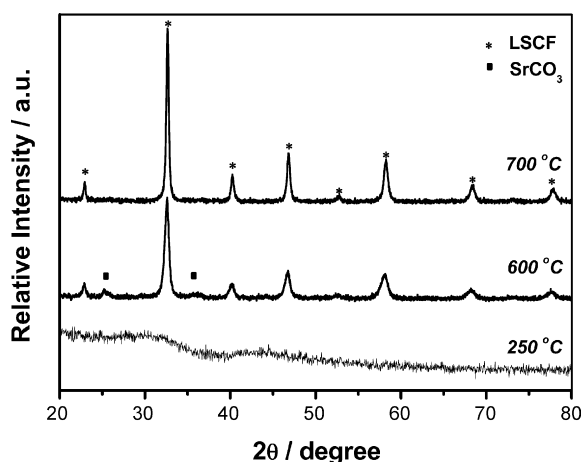


Fig. 4. X-ray diffraction patterns of the LSCF-CE combined complex precursor after pyrolysis (250 °C) and calcinations at 600 °C or 700 °C.

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 reproductive 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:

$$d_{\text{BET}} = \frac{6}{\rho S_v} \quad (1)$$

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 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} 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 $\log(\sigma T)$ as a function of $10^3/T$ from 20 °C to 1000 °C for the three LSCF samples. The measured electrical conductivity for each sample increased with increasing temperature, reached a

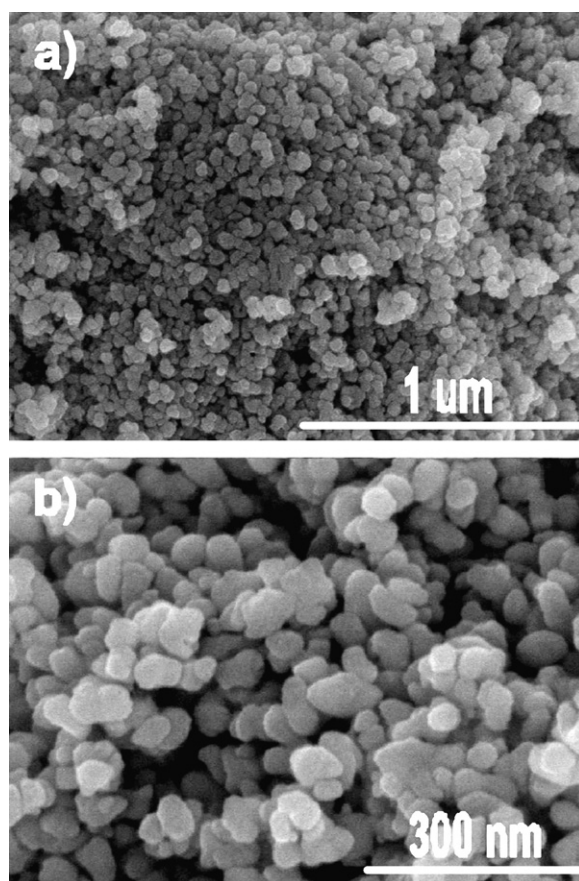


Fig. 5. FESEM micrograph of the LSCF-CE combined complex precursor after calcination at 700 °C at (a) low magnification and (b) high magnification.

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 214 S cm⁻¹ at 500 °C, 284 S cm⁻¹ at 700 °C and 276 S cm⁻¹ at 700 °C,

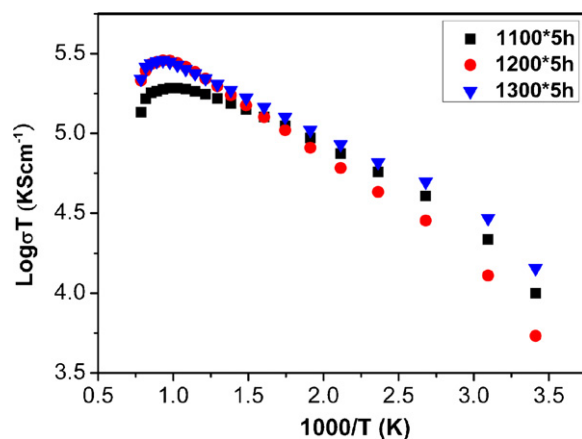


Fig. 6. Plot of $\log(\sigma T)$ as functions of $10^3/T$ for synthesized La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} pellets sintered at 1100 °C, 1200 °C, 1300 °C for 5 h, respectively.

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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ compound were successfully prepared via the modified combined complexing method. Results of the FTIR 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

- [1] N.P. Brandon, S. Skinner, B.C.H. Steele, *Annu. Rev. Mater. Res.* 33 (2003) 183–213.
- [2] D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, *Chem. Soc. Rev.* 37 (2008) 1568–1578.
- [3] S.J. Skinner, *Int. J. Inorg. Mater.* 3 (2001) 113–121.
- [4] A. Mai, V.A.C. Haanappel, S. Uhlenbruck, F. Tietz, D. Stöver, *Solid State Ionics* 176 (2005) 1341–1350.
- [5] L.W. Tai, M.N. Nasrallah, H.U. Anderson, D.M. Sparlin, S.R. Sehlin, *Solid State Ionics* 76 (1995) 273–283.
- [6] L.W. Tai, M.N. Nasrallah, H.U. Anderson, D.M. Sparlin, S.R. Sehlin, *Solid State Ionics* 76 (1995) 259–271.
- [7] V. Dusastre, J.A. Kilner, *Solid State Ionics* 126 (1999) 163–174.
- [8] S.P. Jiang, *Solid State Ionics* 146 (2002) 1–22.
- [9] W.G. Wang, M. Mogensen, *Solid State Ionics* 176 (2005) 457–462.
- [10] M.P. Pechini, US Patent 3,330,697 (1967).
- [11] W. Zhou, Z.P. Shao, R. Ran, H.X. Gu, W.Q. Jin, N.P. Xu, *J. Am. Ceram. Soc.* 94 (2008) 1155–1162.
- [12] B.L. Cushing, V.L. Kolesnichenko, C.J. O'Connor, *Chem. Rev.* 104 (2004) 3893–3946.
- [13] A. Galenda, M.M. Natile, V. Krishnan, H. Bertagnolli, A. Glisenti, *Chem. Mater.* 19 (2007) 2796–2808.
- [14] D. Berger, C. Matei, F. Papa, G. Voicu, V. Fruth, *Prog. Solid State Chem.* 35 (2007) 183–191.
- [15] S. Guntuka, S. Banerjee, S. Farooq, M.P. Srinivasan, *Ind. Eng. Chem. Res.* 47 (2008) 154–162.
- [16] J. Spooren, A. Rumpelcker, F. Millange, R.I. Walton, *Chem. Mater.* 15 (2003) 1401–1403.
- [17] Z.P. Shao, W.S. Yang, Y. Cong, H. Dong, J.H. Tong, G.X. Xiong, *J. Membr. Sci.* 172 (2000) 177–188.
- [18] W. Zhou, Z.P. Shao, W.Q. Jin, *J. Alloys Compd.* 426 (2006) 368–374.
- [19] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co., London, 1954.
- [20] H.A. Szymanski, *Interpreted Infrared Spectra*, vol. 2, Plenum Press, New York, 1966.
- [21] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*, Wiley, New York, 1997.
- [22] M. Matzapetakis, C.P. Raptopoulou, A. Tsohos, B. Papefthymiou, N. Moon, A. Salifoglou, *J. Am. Chem. Soc.* 120 (1998) 13266–13267.
- [23] M. Matzapetakis, C.P. Raptopoulou, A. Terzis, A. Lakatos, T. Kiss, A. Salifoglou, *Inorg. Chem.* 38 (1999) 618–619.
- [24] M. Dakanali, E.T. Kefalas, C.P. Raptopoulou, A. Terzis, T. Mavromoustakos, A. Salifoglou, *Inorg. Chem.* 42 (2003) 2531–2537.
- [25] S. Liu, K. Li, R. Hughes, *Mater. Res. Bull.* 39 (2004) 119–133.
- [26] M. Kakihana, M. Yoshimura, *Bull. Chem. Soc. Jpn.* 72 (1999) 1427–1443.
- [27] R.A. Rocha, E.N.S. Muccillo, *Chem. Mater.* 15 (2003) 4268–4272.
- [28] Y. Teraoka, H. Zhang, K. Okamoto, et al., *Mater. Res. Bull.* 23 (1988) 51–58.
- [29] M. Kertesz, I. Riess, D.S. Tannhauser, R. Langpage, F.J. Rohr, *J. Solid State Chem.* 42 (1982) 125–129.