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Low temperature synthesis of perovskite oxide using the adsorption properties of cellulose

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$La_{0.8}Sr_{0.2}CoO_3$ (LSCO) oxide powder was prepared using the adsorption properties of cellulose. The preparation process was studied by XRD, FTIR, TG-DTA and CO_2-TPD techniques. The results of XRD, IR and TG-DTA testified that cellulose could successfully reserve the homogeneity of the solution system to the solid precursor. During the early stage of pyrolysis, cellulose was partially oxidized, and some COO^- groups appeared in its texture, which were then complexed with the adsorbed metal ions, and effectively suppressed the aggregation of metal ions. Formation of a pure perovskite and the properties of the powder resulted were found to be significantly influenced by the cellulose to metal nitrate ratio. Also the properties of the resulting powder were greatly influenced by the calcination conditions. If the produced carbon dioxide could not be eluted in time, carbonate would be formed in the bulk. Hence, a high calcination temperature (>800°C) was needed to acquire a pure phase LSCO. At optimized conditions, nano-crystal LSCO could be obtained at as low as 500°C.

1. Introduction

Perovskite-type mixed metal oxides with the structure of ABO_3 (A = lanthanide or alkaline earth metal and B = transition metal) have attracted great attention due to their excellent electric, optical, magnetic and catalytic properties [1–4]. One of the particular interests is strontium-substituted lanthanum cobalt oxide $La_{1-x}Sr_xCoO_3$, which find applications in the catalytic decomposition of environmental pollutant NO_x [5], and the oxidation of carbon monoxide, ammonia, methane and other light hydrocarbons [6–9]. $La_{1-x}Sr_xCoO_3$ are mixed oxygen ionic and electronic conductors (MIEC's). Partial substitution of La^{3+} by Sr^{2+} increases oxygen vacancies in the oxide bulk, which is the reason for oxygen ionic conductivity. The balance of electric neutrality can also be obtained by converting Co^{3+} to Co^{4+}, and the electron hops between Co^{3+} and Co^{4+} leads to electronic conductivity. Therefore, such materials can be fabricated into oxygen permeable membranes, allowing oxygen to permeate at high temperatures without the using of both the electrodes and the outside connecting lines [10, 11]. $La_{1-x}Sr_xCoO_3$ can also be used as an electrode material to reduce interfacial resistance by eliminating the need for a three-phase contact area (gas, electrode, electrolyte) [12]. Large specific surface area is needed for high activity as a catalyst. Powder having high purity, phase homogeneity, narrow particle size distribution and fine crystalline size is required for the preparation of electrodes and dense ceramic membranes. Due to the unavoidable drawbacks of the solid state reaction technique such as high calcination temperatures (resulting in low surface area and easy loss of volatile elements), uncontrollable particle size distribution, lacking of phase homogeneity, as well as impurity introduction, chemical methods are extensively used. New methods have been developed, such as sol-gel and coprecipition techniques [13–17]. Those methods can make the reactants to be mixed in the molecular level, thus eliminating the diffusion barrier during calcination, so that materials with homogeneous phase composition, fine particle size and high specific surface area can be obtained at lower temperatures. Pyrolysis of salt-cellulose composition is a recently developed synthesis method, which has been found to be effective for preparing mixed metal oxides. For example, it was found that the temperature for the densification of YSZ ceramic materials prepared by pyrolysis of a metal-oxalate-cellulose complex was much lower (more than 300°C) than that required in a conventional procedure [18].

In this paper, we report the successful synthesis of perovskite-type nano-crystal sized $La_{0.8}Sr_{0.2}CoO_3$ (LSCO) by the pyrolysis of a cellulose-metal compound at a low temperature. Investigation was made on the roles of cellulose during different stages of the preparation process. The influence of the ratio of cellulose to metal nitrates on the phase formation and characteristics of the resulted powders were also investigated.

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The burning behavior of the solid precursor was also studied. In addition, the influence of calcination conditions on the phase formation was also investigated by applying XRD and CO_2-TPD techniques.

2. Experimental

Analytic agents of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and HNO_3, and cotton fiber were used as the starting materials. The cotton fiber was pretreated by concentrated HNO_3 at room temperature for about half an hour. The preparation route of the LSCO is schematically illustrated in Fig. 1. $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Co(NO_3)_2 \cdot H_2O$ were first made into aqueous solutions respectively, their precise concentrations were determined by the EDTA titration method. The metal nitrate solutions were then mixed in stoichiometric amounts. The volume of the mixed solution was adjusted to a certain value, then the pretreated cellulose material was added. The whole system was vibrated vigorously to make the metal salts to adsorb on the cellulose surface evenly and sufficiently. Later, some HNO_3 was added into the system, then it was heated at 50°C in a closed container for several hours, finally heated at 80°C open to the air to evaporate the water. A solid precursor was obtained with the color of hydrated cobalt ions, which was easily to be pulverized. The precursor was fired at different temperatures for several hours in a muffle oven under a static air atmosphere. The heating rate was 10°C/min. Usually a small amount of precursor was used for the pyrolysis study, and the crucible for holding the precursor was open to the air in order to ensure sufficient oxygen supply and free elution of produced carbon dioxide during pyrolysis. The above-mentioned pyrolysis condition is used for the pyrolysis study throughout this paper, unless it was specially referred.

XRD characterization was carried out using a Rigaku D/Max-RB X-ray diffractometer with Cu K_α radiation at 40 KV × 100 mA from 10° to 80° for crystalline phase detection. IR spectra of raw materials, the precursor and the resulting products fired at various temperatures were performed at a Nicolet Impact 410 FT-IR spectrometer. Thermal gravimetry and differential thermal analysis (TG-DTA) were performed with a Perkin-Elmer TGS-2 and a DTA 1700 instruments. Air was used as the carrier gas at a flow rate of 30 ml/min, the heating rate was monitoring at 10°C/min. CO_2-TPD study was conducted in a homemade multipurpose temperature-programmed apparatus. Helium was used as the carrier gas at a flow rate of 20 ml/min. Thermal conductivity detector (TCD) was used for the eluted carbon dioxide detection. Computer was used for data acquisition and processing. Before the CO_2-TPD experiment, the samples were predried at 100°C, the amount of sample was about 100 mg. An inorganic absorbent was used for the adsorption of possible water production. The contents of carbon residue in the samples were calculated from the areas of CO_2 desorption peaks using $SrCO_3$ as the standard substance.

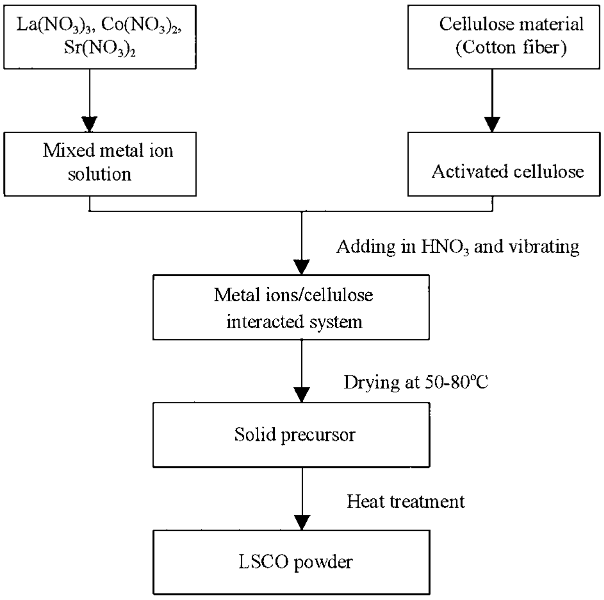

Figure 1 Flow chart for the preparation of $La_{0.8}Sr_{0.2}CoO_3$ powder by the cellulose adsorption method.

3. Results and discussion

3.1. The role of cellulose from mixed solution to solid precursor

To reach mixing of the reactants in the molecular level, the simplest method is to dissolve the metal salts in a mixed solution. But the homogeneity of the solution cannot be reserved during the evaporation of water due to the segregation of metal salts [2]. Some polymers can enhance the homogeneous mixing of the metal cations, and also to suppress the crystallization of metal nitrates. Take PEG as an example, there is ether-oxygen in its chain, and it can interact with metal cations [19]. The interaction and the random arrangement of the polymer chains can effectively hinder crystallization during the evaporation of water from the mixed solution, and thus enhance mixing of metal ions on the molecular level. Cellulose as a polymer, there are abundant R-OH bonds and R-O-R bonds in its molecular structure (three hydroxyl groups and two ether groups in every structure unit). The lone electron pairs in the ether-oxygen atoms and hydroxyl-oxygen atoms can interact with the vacant orbits of metal ions. So it can be a possible candidate substance for the enhancement of the homogeneity of metal ions in the solid precursors.

The temperature for the formation of a pure phase composite oxide is greatly influenced by the degree of mixing level of reactants. Usually, the higher the mixing level of the reactants, the less diffusion obstacle is needed to overcome during firing, so a lower firing temperature can be employed. In order to investigate the addition of cellulose in the enhancement of the homogeneity in the solid precursor and the influence on the properties of the resulting powder, different ratios of cellulose to metal nitrates were tried. Fig. 2 shows the XRD profiles of powder products by firing precursors at 600°C for 2 h which contained 29.86 mmol $La(NO_3)_3$, 37.325 mmol $Co(NO_3)_2$, 7.465 mmol $Sr(NO_3)_2$ and different weight contents of cellulose (10 g, 20 g, 30 g, 40 g, 50 g). As expected, the calcined product whose

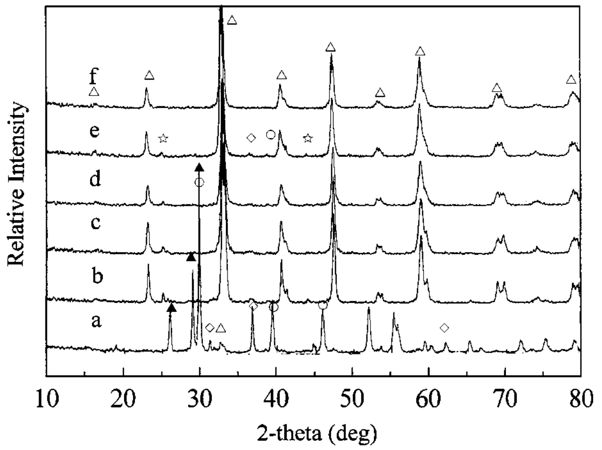

Figure 2 XRD profiles of products fired at 600°C for 2 h, whose precursors contained 29.86 mmol $La(NO_3)_3$, 37.325 mmol $Co(NO_3)_2$, 7.465 mmol $Sr(NO_3)_2$ and different weight contents of cotton fiber. (a) 0 g, (b) 10 g, (c) 20 g, (d) 30 g, (e) 40 g, (f) 50 g. △: perovskite, ▲: La_4SrO_7, ☆: $SrCO_3$, ○: La_2O_3, ◇: Co_3O_4.

precursor contained no cellulose was mainly composed of La_2O_3, La_4SrO_7, Co_3O_4 and some unidentified phases, and only a trace of perovskite phase was detected. But for the calcined products whose precursors contained cellulose, the results of XRD determination indicate that the basic structure of the perovskite was fully formed, demonstrating that the cellulose indeed could enhance the homogeneity of metal cations in the solid precursor. A pure phase perovskite LSCO was acquired for the precursor containing 50 g cellulose, but for the others, some weak other phases (mainly $SrCO_3$) were observed. The intensities of minor phases increased with the decrease of the cellulose content in the precursor. The optimized weight of cellulose needed to above-mentioned moles metal salts was about 50 g. The crystalline sizes of the products (see Table I) were estimated according to the broadening of x-ray diffraction-line using the scherrer equation $D = k\lambda / B \cos\theta$, where D is the crystalline size (nm), λ is the wavelength of Cu K_α radiation (nm), and B is the calibrated width of diffraction peak (200) at half-maximum intensity (rad). It shows that the crystalline size decreased with the increase content of the cellulose. It might be due to the fact that the more cellulose was used, the higher dispersity of metal ions was on cellulose surface, so the less possibility was for the oxide products to aggregate. In the later experiment all the study was conducted on the precursor contained the optimized cellulose to metal nitrates ratio.

The resulting solid precursor exhibited the color of hydrated cobalt ions, which indicated the existence of interaction between cobalt and hydroxyl groups. The results of TG show that the final powder (pure perovskite oxide) was 13.0 wt% of the original solid precursor. The theoretical gain was 12.9% assuming there were no free water present in the solid precursor. These results agree well with each other, demonstrating that the color of hydroxyl cobalt ions was indeed due to the interaction between cobalt ions and hydroxyl groups in the cellulose chain. XRD diffraction pattern of the metal-cellulose precursor was similar to that of the activated cellulose (As shown in Fig. 3), and is designated as the α-type cellulose. No indicative peaks of metal nitrates were detected, suggesting that the metal salts were dispersed on the cellulose surface very homogeneously.

TABLE I Crystalline size along 200 mirror of the calcined samples at 600°C for 2 h whose precursors contain different weight cellulose

Cellulose weight (g)	10	20	30	40	50
Crystalline size (nm)	39.2	34.0	27.0	20.0	19.6

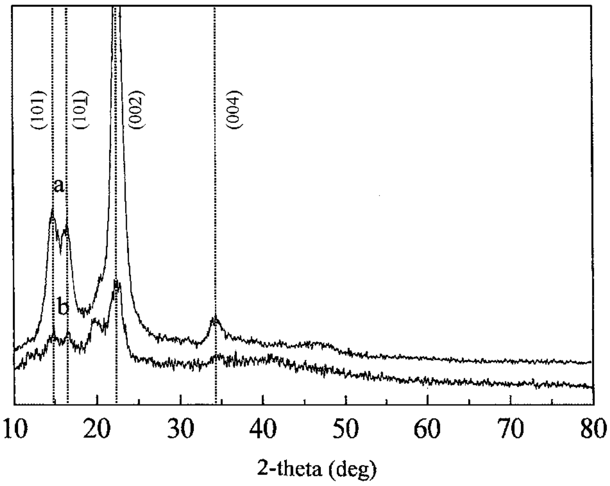

Figure 3 XRD profiles of (a) α-cellulose, (b) precursor that contained 50 g cotton fiber.

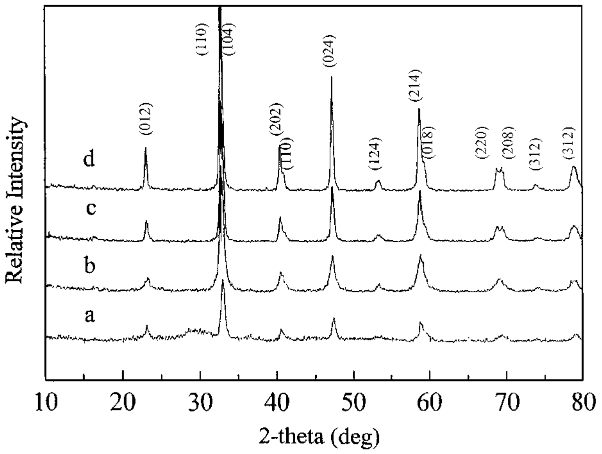

Figure 4 XRD profiles of precursor that contained 50 g cotton fiber and fired at different temperatures for 2 h under static atmosphere and sufficient oxygen supply. (a) 400°C, (b) 500°C, (c) 600°C, (d) 800°C (the mirror numbers indexed was based on the rhombohedral perovskite structure).

3.2. Pyrolysis behavior of the precursor

Fig. 4 shows the XRD profiles of the precursor fired at various temperatures for 2 h. The basic perovskite structure was formed for the product calcined at 400°C. All diffraction peaks were completely indexed as the perovskite-type structure for the sample calcined at 500°C. The corresponding CO_2-TPD results were shown in Fig. 5. A sharp desorption peak appeared around 600°C for the sample calcined at 400°C, and the easy re-decomposition of the carbonate indicated

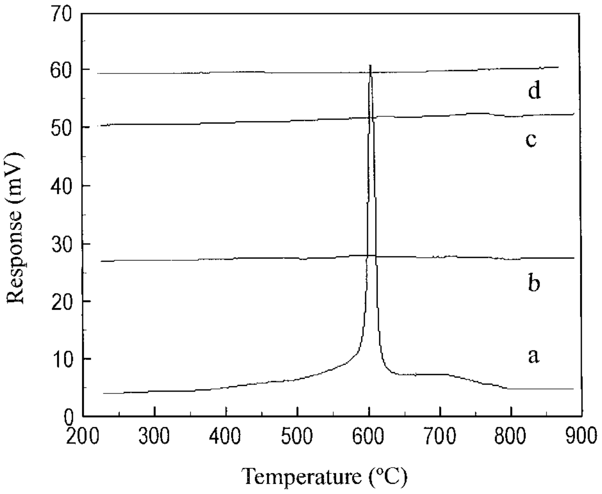

Figure 5 CO_2-TPD profiles of samples calcined at different temperatures for 2 h. (a) 400°C, (b) 500°C, (c) 600°C, (d) 800°C.

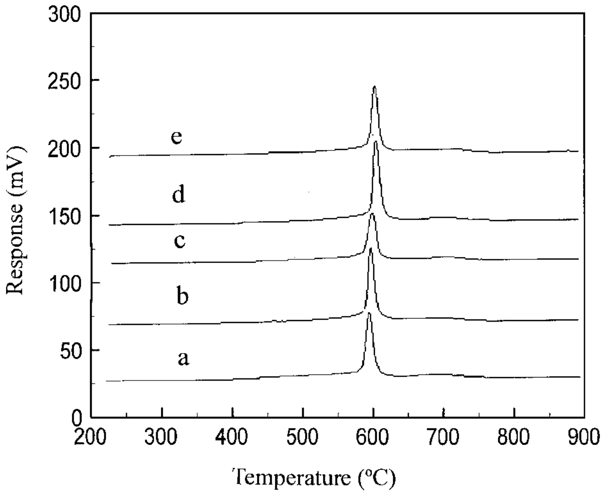

Figure 6 CO_2-TPD profiles of samples calcined at 400°C for different hours. (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 10 h.

that the carbonate was highly dispersed in the bulk oxides. Weak but certainly existing CO_2 desorption peaks were observed for the samples calcined at 500°C and 600°C respectively. Due to the high dispersity and minor amount, the carbonate residue was undetectable by the XRD technique, but was easily detected by the CO_2-TPD technique because of the high sensitivity of TCD. Hardly any eluted CO_2 was detected for the sample calcined at 800°C for 2 h. Using pure $SrCO_3$ as a standard substance for carbon dioxide, the amounts of carbon residue in the samples can be calculated from the eluted CO_2, and the results were listed in Table II. It has been pointed out that the carbon residue from the organic-metal precursor could counteract largely the advantages of low temperature processing [20]. The results of CO_2-TPD show that the temperature sensitive for carbonate formation was lower than 400°C, so a direct calcination temperature higher than 400°C was preferable. In order to investigate the effect of calcination time on the carbon residue, the precursor was fired at 400°C for various hours, then the products were studied by the CO_2-TPD technique, and the results were shown in Fig. 6. For all the samples, carbon dioxide desorption peaks were observed. The amounts of calculated carbon residue and peak temperatures of desorption were listed in Table III. The results demonstrated that it was in vain to get rid of the carbonate residue by trying to prolong the calcination time at 400°C. On the contrary, desorption peaks shifted slightly to a higher temperature zone with the increase of calcination time, which indicated the growth of crystalline size of the carbonate, and so higher calcination temperatures were necessary to get rid of it.

TABLE II Carbon residue of samples calcined at different temperatures, calculated from CO_2-TPD

Temperature (°C)	400	500	600	800
Carbon content (%)	2.17	0.196	0.145	0.019

TABLE III Peak temperatures and calculated carbon residue for the samples calcined at 400°C for different hours

Time (h)	2	4	6	8	10
Peak temperature (°C)	598	603	610	615	614
Carbon content (%)	2.17	2.05	1.86	2.15	2.13

The FTIR spectra of the cellulose, cellulose-metal mixed precursor and products fired at various temperatures are shown in Fig. 7. The IR spectrum of the activated cellulose shown in Fig. 7a exhibited the typical structure of α-cellulose, well in consistence with the XRD result. The broad band around 3450–3300 cm^{-1} was due to the stretch vibration of O-H, while the strong band with a group of peaks around 1150–1000 cm^{-1} was the stretch vibration of C-O-C in the cellulose structure. The peaks around 2990 cm^{-1} and 1370–1340 cm^{-1} were attributed to the νC-H and δ(C-H) + δ(O-H) respectively, and the weak bands around 1648 cm^{-1} and 1420 cm^{-1} were caused by adsorbed water in the cellulose surface and δ(c-H) respectively. The FTIR spectra of the precursor are similar to that of the cellulose, except that a strong peak around 1460 cm^{-1} appeared, and the peak around 1347 cm^{-1} was strengthened, which were attributed to asymmetric

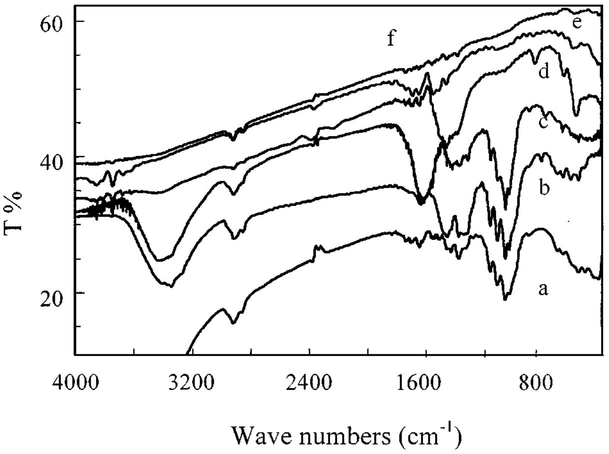

Figure 7 FTIR profiles of (a) α-cellulose, (b) α-cellulose -metal mixed precursor and calcined product firing at (c) 90–190°C for 2 h, (d) 400°C for 2 h, (e) 500°C for 2 h, (f) 800°C for 2 h.

stretch vibration of ν_{as}(O=N=O) of complexed NO_3^- and ν(O=N=O) of ionized NO_3^- respectively. The weak peak around 806 cm^{-1} was the δ(O=N=O) vibration of NO_3^-. The similarity of the FTIR spectra of the precursor and the raw materials indicates that the interaction between cellulose and metal salts did not involve in the change of the cellulose molecular structure. It was a kind of weak chemisorption. Fig. 7c shows the FTIR profiles of samples fired at different temperatures from 90°C to 190°C for 2 h. Compared with the FTIR profile of cellulose, it shows that the basic structure of the cellulose after this treatment was still preserved, but the intensities of the characteristic peaks of NO_3^- at 1347 cm^{-1} and 1460 cm^{-1} were reduced obviously, indicating a reduction of the NO_3^- during this temperature process. Another obvious difference was that a very strong peak occurred around 1630 cm^{-1}, which was the characteristic stretch vibration peak of monodentate complexed COO^- group. So conclusion can be drawn that the NO_3^- group was reduced during the heating treatment between 90–190°C, and the active groups of CH_2OH and C-O-C in the cellulose were partially oxidized to COOH groups, which were then coordinated with the metal salts, but the basic structure was successfully survived during this temperature processing. The formation of metal complexed COO^- in this process helped to suppress the aggregation of metal salts during pyrolysis. The FTIR profile of the sample calcined at 400°C shows that a broad peak around 1467 cm^{-1} and a weak peak around 851 cm^{-1} appeared, which were the characteristic vibrations of carbonate, indicating the formation of carbonate during this temperature process. But for the product calcined at 600°C, all the peaks from 600 cm^{-1} to 4000 cm^{-1} disappeared almost, while a very weak peak around 590 cm^{-1} appeared, the same with the product calcined at 800°C, which was the Co-O stretching vibration of LSCO.

Fig. 8 shows the TG-DTA results of the solid precursor. There was an endothermic peak from 50°C to 90°C in the DTA curve accompanied with a weak weight loss in TG, which was attributed to a minor evaporation of the adsorbed water and HNO_3 and the bond breaking in the organic compound. Around 143°C a sharp exothermal peak occurred with a sharp weight loss in TG. Combining with the IR result, it was attributed to the oxidation of C-O-C and CH_2-OH groups of the cellulose and the reduction of NO_3^-. A broad exothermal peak appeared from 250°C to 360°C accompanied by a second sharp weight loss from 290°C to 320°C in TG, which was due to the burning out of cellulose. There were an endothermic peak around 380°C and an exothermal peak around 400°C with a small weight loss in TG, which were attributed to the decomposition of metal carbonates and the formation of perovskite.

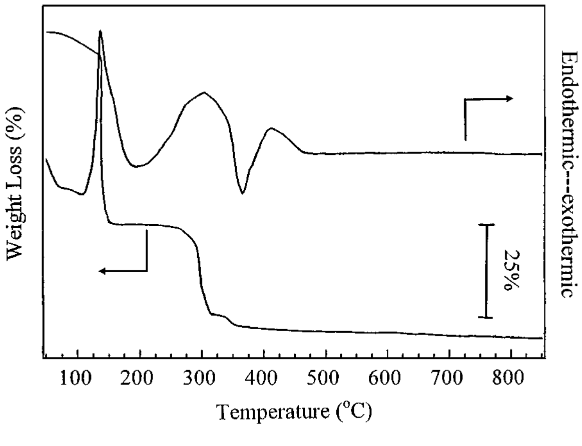

Figure 8 TG-DTA profiles of the precursor contained 50 g cotton fiber.

3.3. Effect of calcination conditions on perovskite formation

One common characteristic of metal-organic precursors is the abundant carbon atoms in them. Provided that all the carbon after pyrolysis was converted into CO_2, H to H_2O, and N to N_2, and the final valence of La, Sr and Co was 3+, 2+ and 3+ respectively, during pyrolysis, considerable amount of oxygen was consumed and large amount of carbon dioxide was produced simultaneously. In the typical experiment, the precursor contained 37.32 mmol $Co(NO_3)_2$, 29.85 mmol $La(NO_3)_3$, 7.46 mmol $Sr(NO_3)_2$ and 50 g cellulose. The structure unit of cellulose is $C_6H_{10}O_5$, so 1.744 mol O_2 is required to burn out 50 g cellulose thoroughly. The decomposition of NO_3^- is only able to provide equal to 0.224 mol O_2, so during the pyrolysis, the system consumes a lot of oxygen and produced abundant carbon dioxide. If the produced carbon dioxide could not be let out in time, the contacting time between the oxides and the produced carbon dioxide were prolonged, so the chance for carbonate formation would increase greatly. Therefore, one key point during the pyrolysis of the precursors was that oxygen must be supplied sufficiently and the produced carbon dioxide must be removed in due time. Fig. 9 shows the CO_2-TPD profiles of samples calcined under the condition in which a relatively large amount of precursor was used and with a cover on the crucible to create a deficiency oxygen supply and a larger contact time between carbon dioxide and the produced oxides. The calcination time was 2 h. A

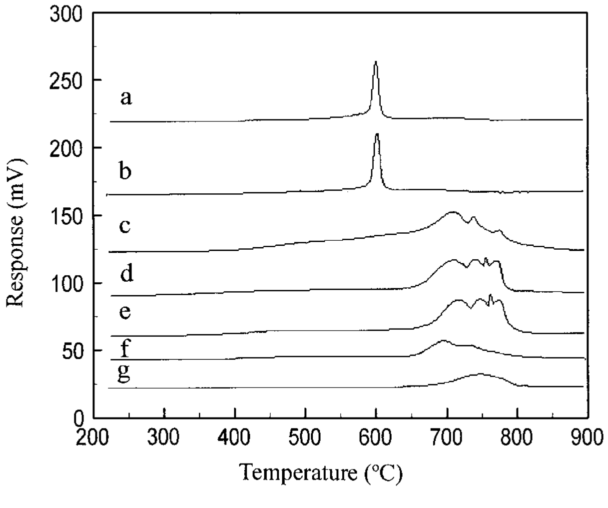

Figure 9 CO_2-TPD profiles of samples calcined at different temperatures for 2 h. (a) 400°C (sufficient oxygen supply), (b) 400°C, (c) 450°C, (d) 550°C, (e) 600°C, (f) 700°C, (g) 800°C. (b–g) Under insufficient oxygen supply.

TABLE IV Carbon residue calculated from CO_2-TPD and TG experiments for the samples calcined at different temperatures under insufficient oxygen supply

Temperatures (°C)	400	450	550	600	700	800
C(%) CO_2-TPD	2.59	7.81	5.80	5.43	2.49	1.34
C(%) TG	2.4–2.9	10.5–13.2	5.2–6.3	5.3–6.2	2.3–3.4	1.4–1.9

sharp desorption peak around 600°C was detected for the sample calcined at 400°C, which is similar to that of calcined at 400°C under the sufficient oxygen supply, only the intensity of the peak was strengthened a little bit. So the produced carbonate was also highly dispersed in the bulk, and it could be easily removed by further calcination at an intermediate temperature (around 600°C). For the samples calcined at temperatures higher than 400°C, the CO_2-TPD peaks shifted obviously to a higher temperature zone, demonstrating the growth of the crystalline size of carbonate obviously. A calcination temperature higher than 800°C was needed to totally get rid of the carbonate. Several desorption peaks were detected for the samples calcined between 450–600°C, which indicated that more than one carbonate species were produced. The calculated carbon residue was listed in Table IV, and the TG results were also presented, which agreed with CO_2-TPD results very well as a whole.

4. Conclusion

The cellulose adsorption method was found to be effective to produce nano-crystal size LSCO at low temperatures. Cellulose could successfully preserve the homogeneity of the mixed solution into the solid precursor. During the evaporation of water, the cellulose acted as an adsorbent, and the metal salt adsorbed on the cellulose surface. During the early stage of pyrolysis, the nitrate was reduced, simultaneously, partial ether groups and hydroxyl groups were oxidized to COOH groups, which were then complexed with metal ions, the formation of coordinated ions successfully prevented the aggregation of the metal ions. Finally, the cellulose was burnt out. A nano-crystal size LSCO powder with the average crystalline size of 19.6 nm was obtained by fired the precursor with optimal metal nitrate to cellulose ratio at 600°C for 2 h. During the pyrolysis, sufficient oxygen supply and easy let out of produced carbon dioxide is important to acquire pure phase perovskite at low temperatures. CO_2-TPD was testified to be an excellent technique to investigate the carbonate residue.

Acknowledgements

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