Preparation of gas-tight strontium-doped lanthanum cobaltate by an aqueous sol–gel process

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Abstract

Gas-tight dense membranes of highly Sr-doped $LaCoO_3$ (such as the composition $La_{0.3}Sr_{0.7}CoO_3$ chosen in this study) are difficult to prepare using usual synthesis processes. This report presents an aqueous sol–gel route using metal acetates as precursors to achieve this goal. Hydrogen peroxide and ammonia are added to the acetates precursor solution to obtain stable sol and xerogel, as well as a homogeneous powder after heat treatment. Thermal analysis and XRD show the presence of $SrCO_3$ and La_2O_3 when the heat treatment temperature of the xerogel is lower than 950 °C. Single phase of cubic perovskite $La_{0.3}Sr_{0.7}CoO_3$ can be obtained after treatment at above 1000 °C. Sintering the cold pressed green compact at above 1100 °C may result in gas-tight samples. It is found that the sintering temperature has a minor influence on the oxygen permeability of a gas-tight membrane.

Keywords: Lanthanum cobaltate; Sol–gel; Dense membrane

1. Introduction

Perovskite-type Sr-doped $LaCoO_3$ ($La_{1-x}Sr_xCoO_{3-\delta}$) dense membrane is particularly interesting for gas separation owing to its high oxygen ionic conductivity as well as its electronic conductivity. It could be used for the separation of air to obtain pure oxygen and nitrogen-enriched air. In fact, it has been shown that highly Sr-doped $LaCoO_3$ is one of the oxygen semi-permeable materials with the highest oxygen permeability [1]. A good gas-tightness is a critical requirement for the application of such kind of membranes. On the contrary, it is an experimental fact, although the reason is not yet clear, that it becomes more and more difficult to prepare gas-tight and crack-free bulk samples with the increase of Sr content. In our laboratory we have tried various preparation methods, such as mechanically mixing of nitrates and pre-sintering followed by sintering, citrate pyrolysis method, and EDTA method. Most of them, however, have failed to produce gas-

tight samples as the strontium content (x) is higher than 0.5. Finally, as will be described below, an aqueous sol–gel route is found to be suitable to prepare highly Sr-doped powders and gas-tight bulk samples as well. It is a modification of the method which was used by Bilger et al. [2] to prepare $La_{0.86}Sr_{0.14}MnO_3$ powders. In this study, a highly doped composition $La_{0.3}Sr_{0.7}CoO_3$ is chosen. Oxygen permeation data of a few samples will also be presented.

2. Experimental

The flow chart of the synthetic procedure is shown in Fig. 1. Metal acetates $Co(CH_3COO)_2 \cdot 4H_2O$ (0.2 mole), $La(CH_3COO)_3 \cdot xH_2O$ (0.06 mole, $x = 0.0083$) and $Sr(CH_3COO)_2$ (0.14 mole) were used as precursors, which were dissolved in H_2O (500 ml; twice distilled). While stirring the solution, H_2O_2 (153 ml; 30%) was slowly added to it. Foaming as well as solution colour changes (from pink to green) were observed. At last the solution became dark green and clear. Then a small amount of ammonia (5.3 ml; 25%) was added to peptize the solution into a stable sol. Stirring was constant for

about 2 h until no foam was observed. By drying the sol at 80–90 °C for about 10 h, a homogeneous dark green "resin" or an xerogel was obtained. After heat treatment in an oven at 220 °C for several hours for drying and the decomposition of some components such as cobalt acetate (see discussion section), the xerogel turned out to be a soft porous product which was then readily crushed into fine powder.

About 40 mg of such powder was taken for a thermal analysis under flowing air (20 ml min^{-1}) by a PL-STA 625 thermal analyzer. The investigated temperature range was from 25 °C to 1300 °C with a heating/cooling rate of 10 °C min^{-1}. The morphology of the powder was observed using an electron scanning microscope (JEOL JSM-35 CF).

Based on the thermal analysis, the powder was calcined for 10 h at 750 °C. This calcination temperature was chosen in pursuit of a reactive sintering later on. The calcined powder was also heat treated at several temperatures from 900 °C to 1200 °C for 5 h for X-ray diffraction analysis. Step scanning was performed using a Philips PW 1370 diffractometer with CuKα radiation, over the range of 2θ from 20° to 80° at steps of 0.04° (2θ).

The calcined powder was milled in an agate mortar by hand and isostatically cold pressed into green compact pellets (16 mm in diameter) with a pressure of 400 MPa for 5 min. Each pellet was heated at 950, 1000, 1050, 1100, 1150 and 1200 °C respectively with a heating rate of 180 °C h^{-1}, sintered at these temperatures for 10 h, and cooled to room temperature at the same
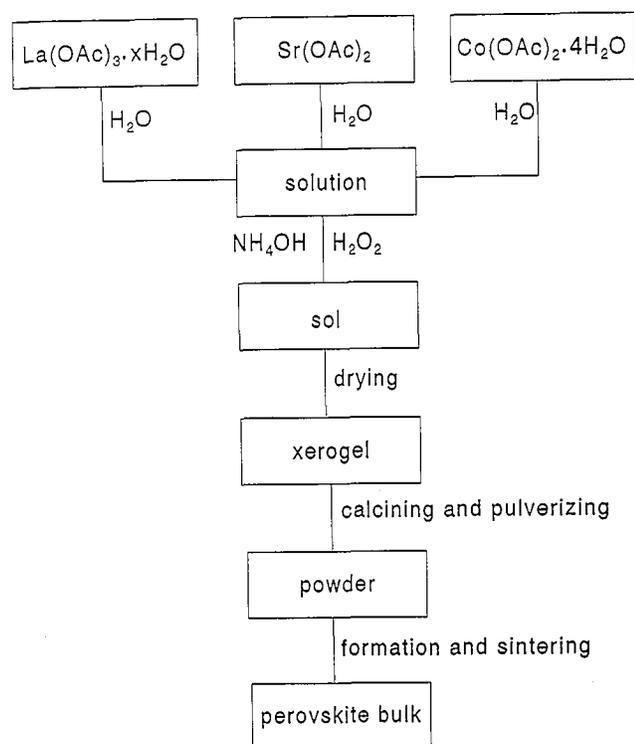

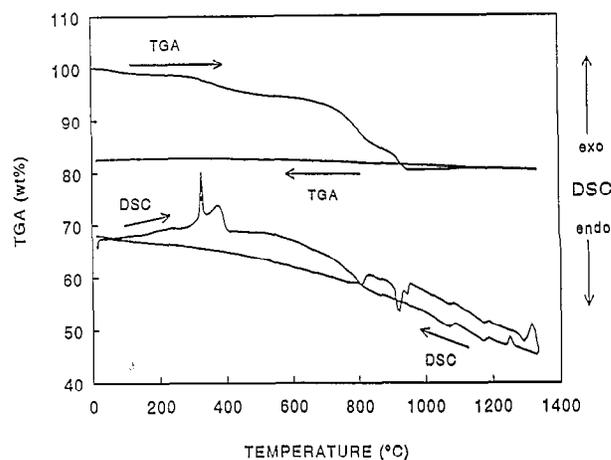Fig. 1. Sol–gel flow chart for the preparation of La$_{0.3}$Sr$_{0.7}$CoO$_3$.

Fig. 2. DSC/TG curves of La$_{0.3}$Sr$_{0.7}$CoO$_3$ powder (after heat treatment at 220 °C).

rate. The sintered pellets shrank to be about 12 mm in diameter. Densities of the samples were measured by the Archimedes method in mercury. Their gas-tightness was detected by a helium permeation cell at room temperature. By applying a gas pressure difference of about 2 bar across a pellet, helium may diffuse to the other side of a non-gas-tight pellet through microcracks and/or pores. The helium leakage flow rate was used to evaluate the gas-tightness in this study. It should be noted that such a room temperature test only gives a good indication about the gas-tightness of a sample. The decisive evaluation on the gas-tightness needed to be done gas-chromatographically in a sealed permeation cell at elevated temperatures. The oxygen permeation measurement was conducted in our set-up over the temperature range of 700–1100 °C. The structure and working principle of the set-up have been described elsewhere [3]. The feed side was flushed with air (60 ml min^{-1}) and the permeation side with pure helium (20 ml min^{-1}).

3. Results and discussion

With regard to this aqueous sol–gel process, hydrogen peroxide used is found to be very important for the sol and xerogel preparations. Before the addition of hydrogen peroxide, acetates are difficult to be dissolved completely in cold water. However, addition of a small amount of hydrogen peroxide, which serves presumably as a complexation agent, together with other ligands (CH$_3$COO$^-$, CO$_3^{2-}$) in the solution, can make the dissolution easily completed. In the course of complexation, the temperature of the solution rose, and CO$_2$ was also detected by gas chromatography. This implies that hydrogen peroxide may also oxidize some acetate groups (CH$_3$COO$^-$) to CO$_3^{2-}$ and CO$_2$. The role of ammonia is to make the solution form a stable sol, but an excess of it will lead to precipitation. The sol is

concentrated during drying, and when the solvent evaporation is nearly finished gelation occurs and a homogeneous xerogel is formed. After calcination, the xerogel is converted to a powder in which the three components are mixed at the molecular level.

Fig. 2 shows the DSC/TG curves of the powder after heat treatment at 220 °C. Naturally, there is not significant thermal effect or mass change occurring below 220 °C except for a small endothermic effect and a small weight loss owing to the desorption of physically adsorbed water. According to the study of Mohamed et al. [4], cobalt acetate has been converted to CoO after the 220 °C treatment. Also, the strong sharp exothermic peak at about 300 °C must correspond to the oxidation of CoO to form Co_3O_4. There follows a lower, broad exothermic peak associated with a small mass loss, but its origin is not quite clear. From 600 °C to 950 °C three endothermic peaks are observed, accompanied by a continuous three-step mass-losses. The total mass loss is about 18 wt.% of the final sample mass of $La_{0.3}Sr_{0.7}CoO_3$. It is just in accordance with 0.7mol CO_2 to 1mol $La_{0.3}Sr_{0.7}CoO_3$. This suggests that the three-step mass loss together with the endothermic peaks probably results from the decomposition of $SrCO_3$ which could be formed during the 220 °C heat treatment of the xerogel. The presence of $SrCO_3$ below 950 °C has been confirmed by XRD analysis, as will be shown below. The onset decomposition temperature of $SrCO_3$ depends on CO_2 partial pressure over the sample, and may be as low as 696 °C when the CO_2 pressure is 0.0335 mmHg [5]. Therefore, the observed decomposition temperature here is reasonable under our experimental conditions. A two-step decomposition of $SrCO_3$ was also observed in N_2 flow [6]. It was ascribed to the increase of CO_2 pressure during decomposition. Nevertheless, in our case the perovskite phase $La_{0.3}Sr_{0.7}CoO_3$ should also be formed in this tempera-

Fig. 4. The relative densities and helium leakage rates of $La_{0.3}Sr_{0.7}CoO_3$ pellets sintered at different temperatures.

ture range because no other thermal (DSC) signals are observed above this range, except for an endothermic peak starting around 1260 °C which is owing to the melting of the perovskite. In addition, the broad peak appearing just below 400 °C is believed to be the result of the oxidation of a lanthanum organic compound to form La_2O_3, the presence of which has also been confirmed by XRD (see below). On cooling, an exothermic peak in the DSC around 1250 °C may be ascribed to the solidification of $La_{0.3}Sr_{0.7}CoO_3$ melt. The small difference of about 10 °C is owing to under-cooling in the solidification process. Note that, the apparent thermal effect between 1070 °C to 1200 °C originates from Al_2O_3 reference for thermal analysis.

The observation by a scanning electron microscope indicates that the powder treated at 220 °C consists of agglomerates of irregular shapes, and has a broad particle size distribution. This is typical for powders produced by aqueous sol–gel routes, and is also analogous to the powder obtained from citrate pyrolysis. Fig. 3 gives the XRD patterns of the powders heat treated at different temperatures. It can be seen that the powder treated at 750 °C shows broad XRD lines of the perovskite phase, together with diffraction lines from small amount of $SrCO_3$ and La_2O_3. With increasing temperature, the perovskite lines become sharp, and the lines of $SrCO_3$ and La_2O_3 gradually disappear at about 1000 °C. Apparently, the decomposition of
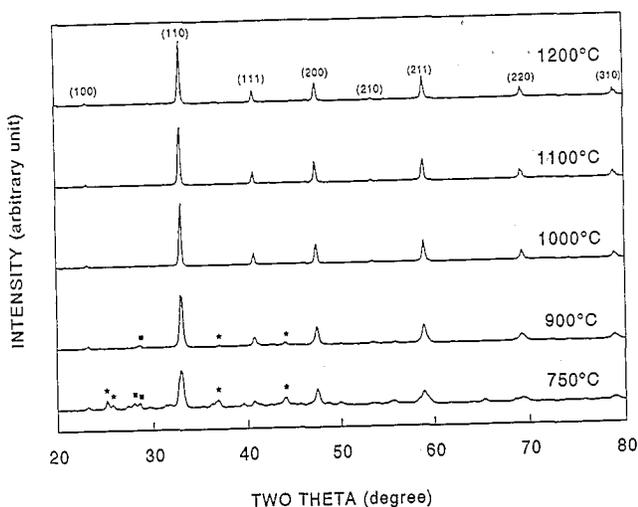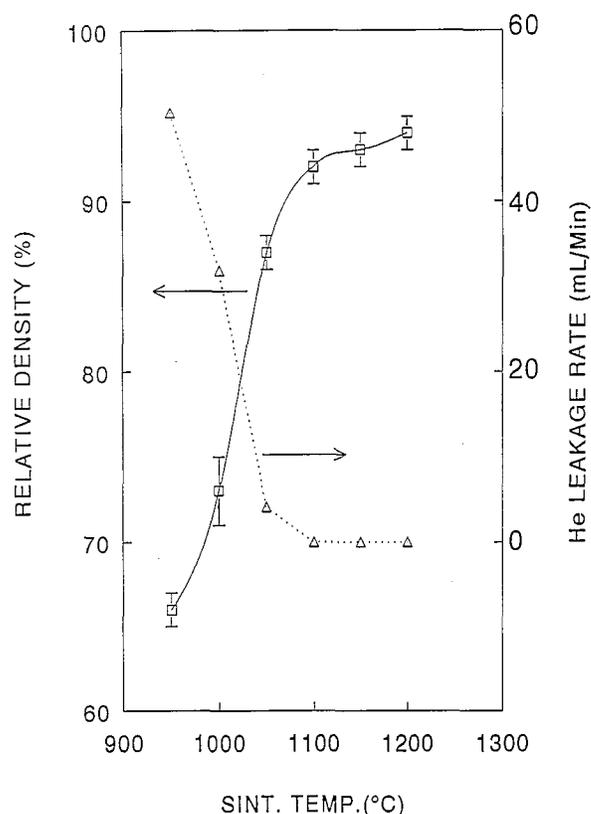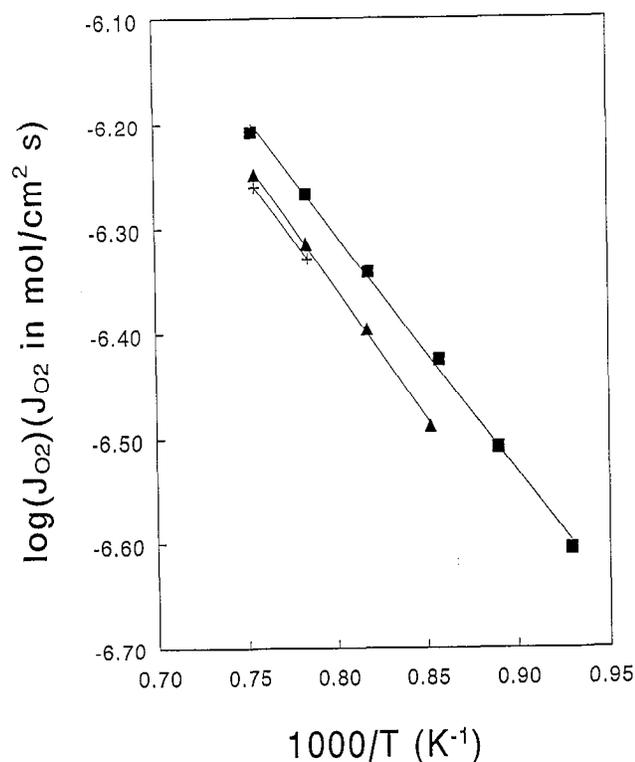

Fig. 3. X-ray powder diffraction patterns of $La_{0.3}Sr_{0.7}CoO_3$ powders calcined at different temperatures. Asterisks (*) give the XRD lines of $SrCO_3$, and squares (■) the XRD lines of La_2O_3.

Fig. 5. The temperature dependence of the oxygen permeability of three $La_{0.3}Sr_{0.7}CoO_3$ pellets sintered at 1100 (■), 1150 (+) and 1200 °C (▲).

$SrCO_3$ and the completion of the solid state reaction to form $La_{0.3}Sr_{0.7}CoO_3$ perovskite phase take place in this temperature range. This is in agreement with the analysis of the DSC/TGA curves. The perovskite patterns can be indexed by a cubic phase, which gives the lattice length of a unit cell $a = b = c = 3.84$ Å, and the theoretical density is therefore determined to be 6.16 g cm^{-3}.

The relative densities and helium leakage rates at room temperature for the pellets sintered at different temperatures are given in Fig. 4. It can be seen that the samples sintered at temperatures lower than 1100 °C are gas-through with relative densities of 67%–87%, and cannot be used as dense membranes for producing pure oxygen. The samples sintered at 1100, 1150 and 1200 °C have relative densities of more than 90%, and are gas-tight (at least at room temperature). It has been also found that, after sintering at a temperature higher than 1000 °C, the surface of a $La_{0.3}Sr_{0.7}CoO_3$ pellet looks smooth and exhibits a metallic appearance, and some melt traces on the alumina plate used as sample susceptor for sintering could be seen. It can be presumed that some extent of liquid phase sintering may occur and lead to a segregation of some component. Increasing oxygen partial pressure in the sintering atmosphere can avoid or reduce the liquid phase sintering. This is worthy of a further investigation.

Fig. 5 shows the temperature dependence of the oxygen permeability (normalized to the feed side area, i.e. $6^2\pi$ mm^2) of three gas-tight pellets sintered at 1100, 1150 and 1200 °C. Obviously, the measured permeability is quite high, up to 6×10^{-7} mol O_2 cm^{-2} s. Within experimental error, the sintering temperatures between 1100–1200 °C hardly affect the oxygen permeability. However, samples sintered at 1150 and 1200 °C sometimes show micro-cracks and are not always completely gas-tight. Therefore, we think that 1100 °C is the optimal sintering temperature.

4. Conclusion

(1) An aqueous sol–gel process has been developed to prepare dense $La_{0.3}Sr_{0.7}CoO_3$ ceramics, which can potentially be used as oxygen semipermeable dense membranes for gas separations.

(2) Thermal analysis and XRD have shown that $SrCO_3$ and La_2O_3 exists in a powder calcined at low temperatures (lower than 900 °C). $SrCO_3$ likely decomposes in the temperature range from 750 to 1000 °C. Single phase of cubic perovskite $La_{0.3}Sr_{0.7}CoO_3$ may be formed at a temperature between 1000 to 1200 °C.

(3) Bulk $La_{0.3}Sr_{0.7}CoO_3$ is gas-tight when it is sintered between 1100–1200 °C. The oxygen permeability of the samples sintered in this range does not show significant difference.

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