Structure and electrical properties of $SrCoO_{3-\delta}$ doped by CeO_2

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Perovskites doped with alkaline-earth metals and transition metals or with A-site substitution by rare-earth elements have been the subject of much research [1]. Stoichiometric ABO_3-type perovskites, such as $La_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xNi_{1-y}Fe_yO_3$ have been successfully used as cathode materials for solid oxide fuel cells (SOFCs). These easily prepared materials have a stable structure during operation and excellent electrical and catalytic properties at high temperature. In some cases, however, their electrical and catalytic performances are not good enough at intermediate or low temperatures. Recently, new kinds of nonstoichiometric perovskite compounds have been found to have potential for use in many fields including SOFCs. According to the literature, these compounds can be used as oxygen permeability films and so on [2, 3]. Only a few reports have been published on nonstoichiometric perovskite compounds as cathode materials for SOFCs. In these papers, Hashimoto *et al.* [4] reported the structure and performance of doped $SrMnO_{3-\delta}$, indicating that $Sr_{1-x}Ce_xMnO_3$ $(0 \le x \le 0.3)$ has a stable cubic structure from high temperature to room temperature. The conductivity of $Sr_{0.7}Ce_{0.3}MnO_3$ reached 290 S/cm at 1000 °C, which is higher than that of $La_{0.8}Sr_{0.2}MnO_3$ (175 S/cm) at the same temperature. The conductivity of the Sr-Ce-Co-O system was thoroughly discussed by Trofimenko *et al.* [5], and the peak value of conductivity, 500 S/cm was obtained at 400 °C according to their report, which demonstrated the possibility of Ce-doped $SrCoO_{3-\delta}$ being used at intermediate or low temperatures.

Undoped $SrCoO_{3-\delta}$ exhibits high concentrations of ionic vacancies; meanwhile it also shows phase instability [6]. The transformation from cubic to orthorhombic symmetry occurs during cooling after sintering, which causes a severe degradation in electrical properties. It is revealed from the previous reports that the doping of CeO_2 inhibits the structural change, so as to maintain the high-temperature cubic symmetry to room temperature. $SrCoO_{3-\delta}$ is one of the compounds with oxygen vacancies that has an ionic conductivity much higher than that of the ABO_3 stoichiometric compound. Nonstoichiometric $SrCoO_{3-\delta}$ stabilized by CeO_2, as a candidate cathode for intermediate temperature SOFC use, was prepared by conventional solid state reaction. Phase formation and structure of the synthesized materials and their electrical properties were investigated and are discussed in this paper.

$Sr_{1-x}Ce_xCoO_{3-\delta}$ ($x = 0.05, 0.10, 0.15, 0.20$) materials were prepared by a solid-state reaction method, using $SrCO_3$ (Tianjin Yuanli Chemical Co, Ltd, 99%), CeO_2 (Shanghai Yuelong Nonferrous Metal Co. Ltd, 99.99%) and Co_2O_3 (Tianjin Yuanli Chemical Co, Ltd, 99%) as raw materials. They were mixed in a stoichiometric molar ratio, and reacted at 800 or 1100 °C for 4 hr in air. After cooling to room temperature, the powder calcined at 1100 °C was crushed and ball-milled again for 12 hr. The powders were pressed into rectangular bars and then sintered at 1100, 1150 or 1200 °C for 4 hr, respectively.

X-ray diffraction (XRD) analyses were carried out to determine the phase composition, using Cu K_α radiation (BDX3300, Beijing). Thermal gravity – differential scanning calorimetry (TG-DSC) was performed using a NETZSCH STA 499C Instrument in air to investigate the phase formation and transformation. The conductivity was measured by DC four-probe method.

For a stable perovskite compound ABO_3, ionic radii must fit the equation as follows

$$r_A + r_B = t\sqrt{2}(r_B + r_O)$$

where, r_A is the ionic radius of A, r_B is the ionic radius of B, r_O is the ionic radius of O and t is the Goldschmidt number, which lies between 0.77 and 1.10. The values of t corresponding to $Sr_{1-x}Ce_xCoO_{3-\delta}$ with different x were calculated using $r(Ce^{4+}) = 0.114$ nm, $r(Sr^{2+}) = 0.144$ nm, $r(Co^{4+}) = 0.061$ nm [6] and listed in Table I.

From Table I, all compositions could form a stable perovskite structure, but the stability showed a trend to decrease slightly with increasing CeO_2 content.

Fig. 1 shows the XRD patterns of $Sr_{1-x}Ce_xCoO_{3-\delta}$ with $x = 0.05, 0.10, 0.15$ and 0.20. According to the standard JCPDS cards, the formed perovskites have tetragonal symmetry, in line with $SrCoO_{3-\delta}$. No CeO_2 phase was detected when x was below 0.15, but it did appear when x reached 0.20, which indicated that the solubility of CeO_2 was between 15 and 20 mol%. With increasing CeO_2 addition, the main peak of perovskites demonstrated a small shift towards larger angles, indicating that the interplanar spacing of the corresponding crystal planes had decreased and that the lattice parameters a and c had also decreased, causing the crystal cell to contract. The changes in the cell parameters and theoretical density (d_0) calculated from the XRD results are listed in Table II.

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TABLE I The value of t with different contents of CeO_2 dopant ($0 \leq x \leq 0.2$)

x	0	0.05	0.10	0.15	0.20
t	0.999	0.994	0.989	0.983	0.978

TABLE II Calculated cell parameters and theoretical density (d_0) from the XRD data

$Sr_{1-x}Ce_xCoO_{3-\delta}$	a (nm)	c (nm)	V (10^{-24} cm^3)	d_0 (g/cm^3)
$x = 0.05$	1.0961	0.7748	930.9	5.42
$x = 0.10$	1.0934	0.7731	924.3	5.56
$x = 0.15$	1.0906	0.7715	917.6	5.70
$x = 0.20$	1.0887	0.7690	911.5	5.84

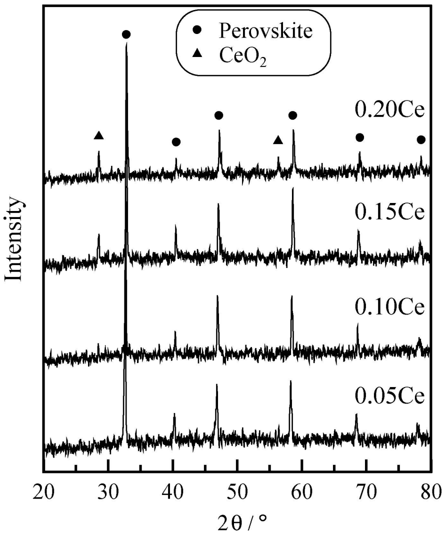

Figure 1 The XRD patterns of $Sr_{1-x}Ce_xCoO_{3-\delta}$ with different amounts of Ce dopant.

The parameters a and c linearly decreased with increasing dopant concentration x; theoretical density increased with x. This could be explained by the increasing amount of ceria with a smaller radius and larger atomic weight.

The transformation of $Sr_{1-x}Ce_xCoO_{3-\delta}$ during cooling from high temperature limits its applications in many fields. This work demonstrates that partial substitution of Sr by Ce can improve the stability, that is to say, that the high-temperature symmetry would remain at room temperature. The results of TG-DSC analyses of $Sr_{0.8}Ce_{0.2}CoO_{3-\delta}$ starting composite powders are given in Fig. 2. The mass loss of 12.7% which occurred in the temperature range of 750–820 °C was attributed to the decomposition of $SrCO_3$. A corresponding sharp endothermic peak appeared at 817 °C, attributed to the formation of low-temperature perovskite phase. The weight loss was very low after 820 °C, suggesting no further decomposition. The weak endothermic peaks at 883 and 993 °C were related to the solution of Ce into A-site and phase transformation to high temperature symmetry, respectively. There were no visible endothermic and exothermic phenomena above 1000 °C, and perovskite structure was completely formed at 1100 °C and remained at room temperature according to the XRD patterns in Fig. 1.

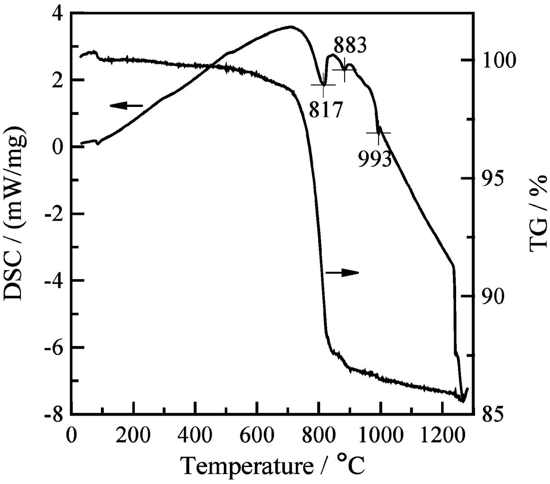

Figure 2 The TG-DSC curves of $Sr_{0.8}Ce_{0.2}CoO_{3-\delta}$ starting composite powders.

Undoped $SrCoO_{3-\delta}$ is a semiconductor. The doping of CeO_2 not only improves its stability, but also changes its conductivity. Of course, the conductivity is also affected by the change of microstructure resulting from doping. The electrical conductivity of $Sr_{1-x}Ce_xCoO_{3-\delta}$ in air is plotted in Fig. 3. All samples were calcined at 800 °C and sintered at 1150 °C. The conductivity of $Sr_{1-x}Ce_xCoO_{3-\delta}$ tended to increase when x varied from 0.05 to 0.15 and to decrease when x was between 0.15 and 0.2. This was caused by the incomplete solution of CeO_2 into $SrCoO_{3-\delta}$, as revealed from the XRD patterns. As an ionic conductor, the existence of CeO_2, as a second phase in $Sr_{0.8}Ce_{0.2}CoO_{3-\delta}$, decreases the conductivity. In the solid solution range where only single phase of perovskite exists, partial substitution of Sr by Ce in $SrCoO_{3-\delta}$ would induce the electric charge imbalance in the system. Trofimenko *et al.* [7, 8] pointed out that the electrical neutrality of this material could be realized by both valence variation of B-site ions and occurrence of oxygen vacancies. Not only oxygen vacancies but also the transition of $Co^{4+} \rightarrow Co^{3+}$ gave rise to the increases in electronic hole and conductivity with increasing amount of CeO_2

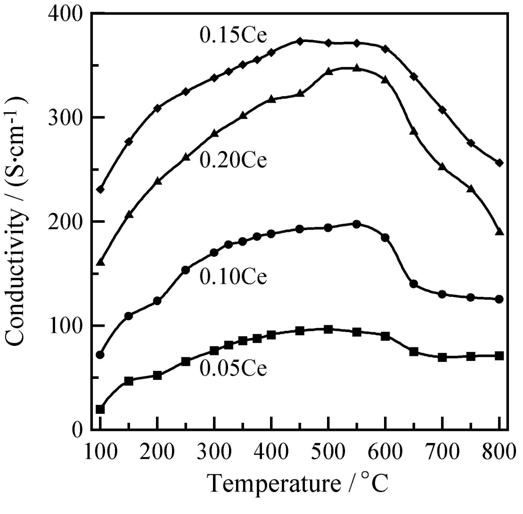

Figure 3 Changes of electrical conductivity with temperature of samples doped with different CeO_2 contents.

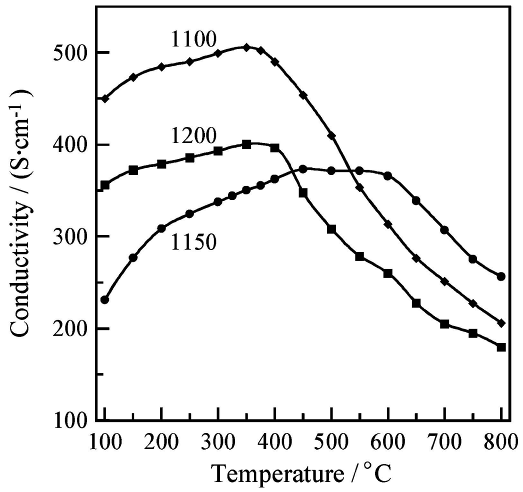

Figure 4 Electrical conductivity of samples with $x = 0.15$ sintered at different temperatures.

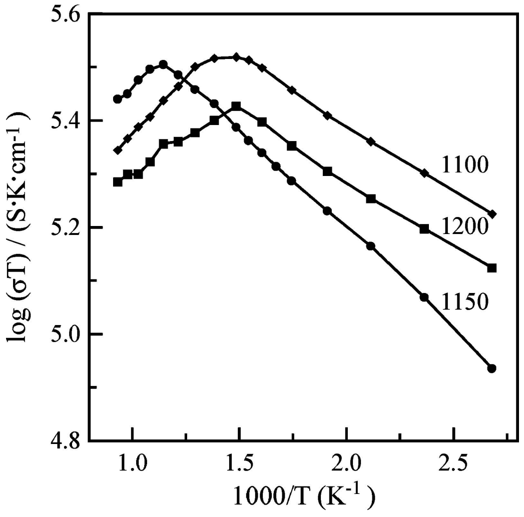

Figure 5 Electrical conductivity as log(σT) versus 1000/T converted from the data of Fig. 4.

dopant. The transition from Co^{4+} to Co^{3+} would be enhanced when $x \geq 0.10$.

The dependence of conductivity of $Sr_{0.85}Ce_{0.15}CoO_{3-\delta}$ on sintering temperature is shown in Fig. 4. It can be seen from the figure that the sample sintered at 1100 °C had the highest value of conductivity. This powder was synthesized at 1100 °C and then ground again, which was believed to be helpful to the formation of perovskite structure and to improve the sinterability. One sample calcined at 1000 °C and sintered at 1200 °C showed a low density, therefore its conductivity was degraded.

Figs 3 and 4 also show the variation of conductivity with testing temperature. In all the curves, conductivity peaks at a temperature of 350–400 °C. The conductivity of the sample sintered at 1100 °C was larger than 500 S/cm. The characteristics of electrical conductance of this material were closely related to its conductive mechanisms varied with temperature. It is a semiconductor at low temperature and a metal-like conductor at intermediate temperature. The small polaron model acts as the predominant conductive mechanism at this range of temperatures. The conductivity decreased with increasing temperature further, resulting from the change of conductive mechanism. For the sample sintered at 1150 °C the conductivity peak drifts to 550 °C and conductivity reduces compared with the sample sintered at 1100 °C, which was caused by the incomplete formation of perovskite during calcination at 800 °C. This would rationally lead to existence of second phases and affect the microstructure and the conductivity as a result.

Data of Fig. 4 are re-plotted by log(σT) vs.1000/T, as shown in Fig. 5. The electrically conductive mechanism at low and intermediate temperatures conforms to the small polaron model and conductivity fits to the equation $\sigma = (\frac{A}{kT})\exp(-\frac{E_a}{kT})$. The activation energy of the samples with 15 mol% CeO_2 are 0.0217 eV at 100–350 °C and 0.0085 eV at 350–400 °C respectively obtained by fitting the data. There was a sharp drop of activation energy at elevated temperatures.

In brief, the structure and electrical properties of $SrCoO_{3-\delta}$ were influenced by doping CeO_2. Sr was partially substituted by Ce, with the solubility limit between 15 and 20 mol%. The stability of $Sr_{1-x}Ce_xCoO_{3-\delta}$ decreased slightly with increasing x, while the crystal cell volume contracted and the theoretical density increased with increasing the dopant. Conductivity of $Sr_{1-x}Ce_xCoO_{3-\delta}$ enhanced with increasing CeO_2 within the solubility limit. The conductivity over 500 S/cm was obtained at $x = 0.15$ when testing at 350–400 °C for the sample sintered at 1100 °C. It meant that this material could fulfill the requirements in electrical properties for applications to low temperature SOFCs.

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