Oxygen Nonstoichiometry and Mixed Conductivity of Doped $LaCoO_{3-\delta}$

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Abstract: Perovskite-type oxides of doped $LaCoO_{3-\delta}$ powders were synthesized by Glycine-Nitrate process (GNP). The powders were characterized by XRD, SEM and laser granularity analysis. The results show that oxides are uniform aggregates with spherical shape and the granularity of aggregates distribute between 0.5~50 μm. The oxygen nonstoichiometry values of the materials were measured by iodometric titration method. The results indicate the oxygen nonstoichiometry of doped $LaCoO_{3-\delta}$ ceramics increase with increasing Co/Fe ratio. The mixed conductivity was investigated by DC four-terminal method, which indicates the cathode materials conductions enhance with the increasing of oxygen nonstoichiometry and temperature, as well as apparent density.

Key words: doped $LaCoO_{3-\delta}$; cathode material of SOFC; oxygen nonstoichiometry; mixed conductivity
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Perovskite-type oxides of doped $LaCoO_{3-\delta}$ with nonstoichiometry have attracted growing attentions for their superior catalytic activity and mixed electronic-ionic conduction properties, which make them promising candidate materials for many important applications, such as cathodes for intermediate temperature solid oxide fuel cells[1-2]. The structures and properties of these oxides were widely discussed and certain results and explanations have been given. Oxygen vacancies are thought to be a major kind of deficiency in perovskite-type oxides, whose concentration and distribution decide the mixed conductivity and catalytic activity of the oxides[3].

However, the complicated effects of the structures on properties of these oxides need furthermore investigation when different cations dope in perovskite structure. In this paper, Sr^{2+} and Ca^{2+} were doped into A site and Fe^{2+} was doped into B site of $LaCoO_{3-\delta}$. Oxygen nonstoichiometry values and mixed conductivity of these oxides were investigated.

1 Experiment

$LaCo_{1-x}Fe_xO_{3-\delta}$ (LCF; x = 0, 0.2, 0.4, 0.6, 0.8, 1) and $La_{0.8}Sr_{0.04}Ca_{0.16}Co_{1-y}Fe_yO_{3-\delta}$ (LSCCF; y = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1) powders were synthesized by Glycine-Nitrate process (GNP)[4]. The powders were characterized via X-ray diffraction (XRD), scan electron microscopy (SEM) and laser granularity analysis. Oxygen nonstoichiometry values of the materials were measured by iodometric titration method. The mixed conductivity was investigated through DC four-terminal method, the powders were pressed into discs then sintered at 1573 K for 4 h. Platinum electrodes were prepared on both sides of the discs. The apparent density was measured by Archimedes method.

2 Results and discussion

2.1 Structure characterization

The XRD results express that all the powders synthesized are perovskite type oxides without any other phase, as shown in Fig.1. The morphology of the powder productions are observed through SEM (Fig.2).

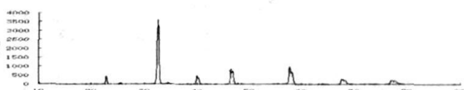

Fig.1 XRD patterns of $La_{0.8}Sr_{0.04}Ca_{0.16}Co_{0.4}Fe_{0.6}O_{3-\delta}$

SEM images indicate the oxides are uniform particles with spherical shape and the aggregate structures of particles can be identified obviously (Fig.2). The re-

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sult of particle size measured by laser granularity analysis was shown in Fig.3. The granularity of aggregates distribute between 0.5 ~50μm.

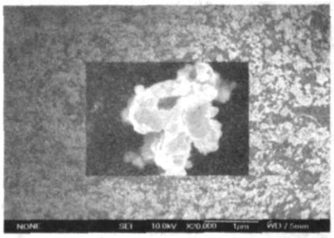

Fig.2　SEM images of $La_{0.8}Sr_{0.04}Ca_{0.16}Fe_{0.8}Co_{0.2}O_{3-\delta}$

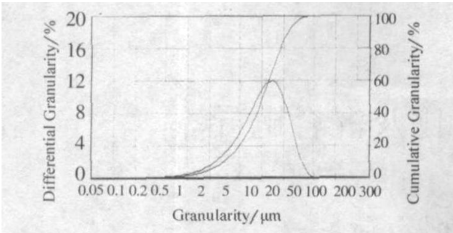

Fig.3　Granularity distributing of LSCCF by laser analysis

2.2　Oxygen nonstoichiometry values

The oxygen nonstoichiometry values of the materials were shown in Fig.4. The values are much higher than those have been reported[5], it seems that the errors brought by manual operation and the method itself should account for that.

In spite of this, the results can still reflect the variation of the oxygen nonstoichiometry values with different doping ion concentration. The results imply oxygen nonstoichiometry values of doped $LaCoO_{3-\delta}$ decrease with increasing doping Fe content. We tentatively interpret this to higher Fe-O bind energy (408.8 ±13 kJ/mol) than Co-O (368 ±21 kJ/mol) and oxygen vacancies formation is difficult in high Fe-content structure. In addition, the Co ions are apt to stay at lower valence state so more oxygen vacancies generate to balance the valence when more Co exist. The δ values of $LaCo_{1-x}Fe_xO_{3-\delta}$ system are usually lower than $La_{0.8}Sr_{0.04}Ca_{0.16}Co_{1-y}Fe_yO_{3-\delta}$ which indicates the Sr^{2+} and Ca^{2+} doped in A site also affect oxygen vacancies concentration significantly.

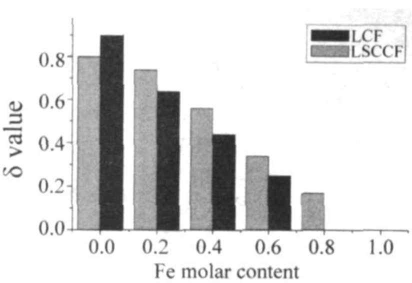

Fig.4　The comparison of non-stoichiometric oxygen of LSCCF and LCF

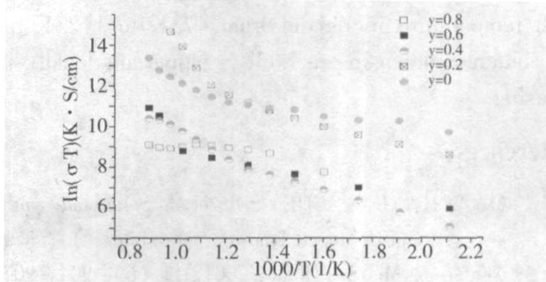

Fig.5　The mixed conductivity of LSCCF and LCF

2.3　Mixed conductivity

The mixed conductivities of LSCCF are investigated by DC four-terminal method. It is shown that the cathode materials conductions are strongly influenced by oxygen vacancies as well as temperature (Fig.5). Just like those of semiconductor materials, the conductivities of LSCCF improve when temperature rose from 473K to 1123K. The conductivities also improved with Co contents increment (more oxygen vacancies), although the effect is not obvious due to the influence by apparent density (Tab.1).

Tab.1　The apparent density of LSCCF

y	δ	Apparent density (g/cm^3)	Mixed conductivity (S/cm, 923K)
1.0	0	4.3575	9.6759
0.8	0.17	4.1264	5.5752
0.6	0.34	4.0492	12.2455
0.4	0.56	5.3836	412.1816
0.2	0.74	5.0261	140.9884

It is observed that samples with higher δ values but lower density may exhibit lower conduction. From the relationship between conductivity and temperature or oxygen vacancies, we confirm the small polaron hopping process[6] in the materials in experiment temperatures range.

3　Conclusions

XRD results indicated that all the powders synthesized are perovskite type oxides without any other phase. SEM images show the particles are uniform aggregates with spherical shape. Granularity of the aggregates measured by laser granularity analysis distribute from 0.5μm to 50μm. Oxygen nonstoichiometry values of $LaCo_{1-x}Fe_xO_{3-\delta}$ and $La_{0.8}Sr_{0.04}Ca_{0.16}Co_{1-y}Fe_yO_{3-\delta}$ decrease with increasing Fe content. Sr^{2+} and Ca^{2+} doping in A site result in increase in δ values. The conductivity of $La_{0.8}Sr_{0.04}Ca_{0.16}Co_{1-y}Fe_yO_{3-\delta}$ improves with temperature increment from 473 K to 1123 K and Co contents increasing as well as apparent density increasing.

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掺杂 LaCoO$_{3-\delta}$的非化学计量比及混合电导率

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摘 要：采用甘氨酸－硝酸盐法（GNP）合成了掺杂钙钛矿型氧化物 LaCoO$_{3-\delta}$系列粉末，并通过 X射线衍射分析、扫描电镜和激光粒度分析等技术对粉末进行了表征。结果表明合成的粉末为均匀、近似球形、粒度在 0.5～50 μm的颗粒团聚体。采用碘滴定法测定了合成氧化物的氧非化学计量值，结果说明氧空位浓度随掺杂铁含量的提高而降低。采用直流四端子法考察了合成材料的混合电导率，结果表明材料的混合电导率随温度、氧空位和密度的提高而提高。

关键词：掺杂 LaCoO$_{3-\delta}$；固体氧化物燃料电池阴极材料；氧非化学计量值；混合电导率

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