Synthesis and Properties of $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ Anode Material by Glycine-Nitrate Process

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Abstract: Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) method was adopted to characterize the reaction process of $La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM7355) anode material by glycine nitrate process. The microstructure and features of LSCM7355 were tested by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), direct current four electrode and temperature process reduction (TPR) techniques. XRD patterns indicates that perovskite phase existed after the precursor was sintered at 1 000 ℃ for 5 h, and LSCM7355 material with single perovskite phase was obtained after sintering at 1 200 ℃ for 5 h. The molar ratio of the elements in LSCM7355 material agrees well with the designed value. The powders have nanometer and micrometer size after sintering at 1 000 ℃ and 1 200 ℃, respectively. The total conductivity of LSCM7355 increases linearly with temperature at air and reaches 25 S/cm at 850 ℃, which wholly becomes smaller in the pure hydrogen and methane.

Key words: $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$; anode material; glycine nitrate process; solid oxide fuel cell; properties
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$LaCrO_3$-based material such as $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM) has high electronic-ionic conductivity, excellently catalytic and reforming properties[1-2]. Maybe many problems[3-4] such as carbon deposition existing in traditional anodes of solid oxide fuel cell (SOFC) can be resolved when LSCM is used as anode material. Therefore, it is necessary that the appropriate conditions were employed to synthesize and characterize these materials.

1 Experimental

$La_{0.7}SrM_{0.3}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM7355) was synthesized by glycine nitrate process (GNP). Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) method were adopted to confirm the synthesis temperature. The powders crystal structure was confirmed using X-ray diffraction (XRD). The size of synthesized material was observed by scanning electron microscopy (SEM). The elements and their percentages in sintered material were characterized by energy dispersive spectroscopy (EDS). The four-probe direct current technique was adopted to measure the total conductivity at different conditions. Temperature process reducing (TPR) experiments was performed too.

2 Results and discussion

2.1 TGA-DSC analysis

Fig. 1 shows the TGA-DSC cures of the precursors of LSCM7355. There is an endothermic peak at about 100 ℃ in the DSC curve, and an initial weight loss of 4.89% below 418 ℃, corresponding to the loss of the bound water. There is an exothermal peak at 418 ℃, the second weight loss of 1.54% between 418 ℃ and 601 ℃ corresponds to the decomposition of the residual nitrate and the elimination of the incomplete glicine combustion. The endothermic peaks at about 601 ℃ and 787 ℃ in the DSC curve corresponding the forming of perovskite phase and their doping process. The changing rate of the thermal weight loss is smooth after 941 ℃. In theory, the LSCM7355 material with perovskite can form above 941 ℃.

2.2 XRD, EDS and SEM of prepared materials

Fig. 2 illustrates the XRD patterns of LSCM7355 powder sintered at 1 000 ℃ and 1 200 ℃ in air, which indicates the perovskite phase together with a little intermediate phase $SrCrO_4$ was produced after sintering at 1 000 ℃ for 5 h. A single-phase perovskite was identified after sintering at 1 200 ℃ for 5 h finally. According to the EDS pattern of LSCM7355 material, there is

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no impurity element other than La, Sr, Cr, Mn and O. The molar ratio of La, Sr, Cr, Mn and O is about 0.7 : 0.29 : 0.53 : 0.45 : 2.18, which is good agreement with the designed value, except a little oxygen shortage. It is suggest that the oxygen vacancies exist in this material.

Fig. 3 shows the SEM images of the LSCM7355 anode materials obtained at different conditions. LSCM7355 powder offer nanometer size after sintering at 1 000 ℃ for 5 h (a). The powder size becomes bigger and about 1 μm after sintering at 1 200 ℃ for 5 h (b). When the LSCM7355 pellet was sintered at 1400 ℃ for 20 h, the most crystalline grains with octahedron shape offers 1.5 ~ 2 μm size (c).

2.3 Conductivity of samples

Fig. 4 shows the conductivity of LSCM7355 at different conditions. The total conductivity of LSCM7355 increases linearly with the temperature at air in the range from 250 ℃ to 850 ℃ and the max value is 25 S/cm at 850 ℃. The conductivity of LSCM7355 becomes smaller when the atmosphere changes from air to pure hydrogen and methane at the same temperature. It is because that the high-valence ionic such as Cr^{4+} or Mn^{4+} was reduced to low-valence one in reducing atmosphere, then the quantity of the small polaron become smaller and its contribution to conductivity decrease. The conductivity of sample in air returns to the initiate value after the cycle, showing excellent reversibility.

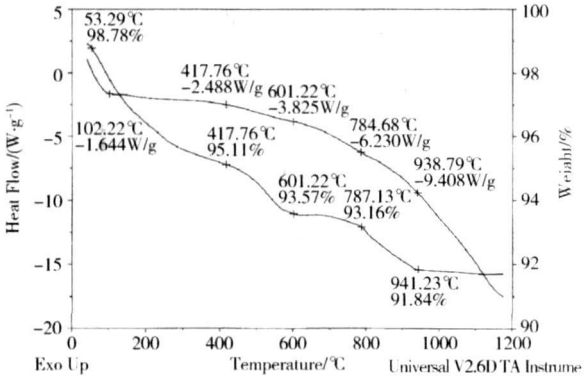

Fig. 1 TGA and DSC curves of the LSCM precursors

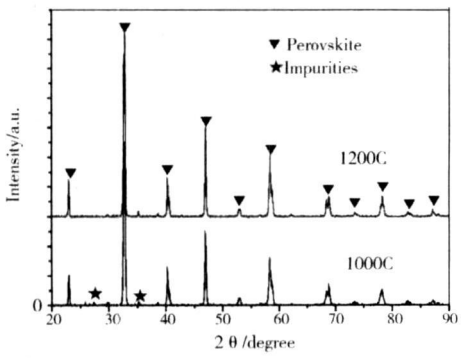

Fig. 2 XRD patterns of LSCM7355 powder

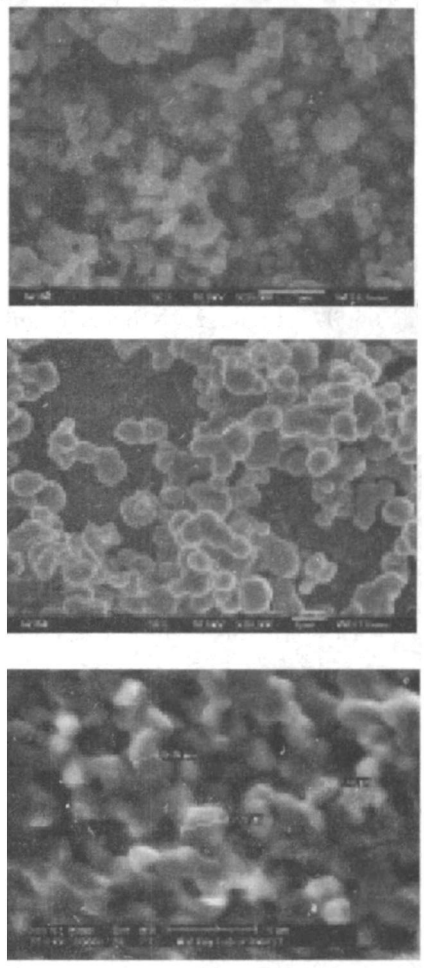

Fig. 3 SEM images of LSCM7355 sintered at 1 000 ℃和 1 200 ℃ and 1 400 ℃ by GNP

Fig. 5 shows the TPR result of LSCM7355. The hydrogen began to be consumed slowly from 200 ℃, corresponding to the absorbed oxygen in the LSCM7355 powder surface. So, the conductivity of LSCM7355 decreases from 250 ℃ in hydrogen. Maxima peak emerged from about 450 ℃, corresponding to the reduction of high-valence metal ionic. So, the LSCM7355 shows the lowest conductivity at about this temperature.

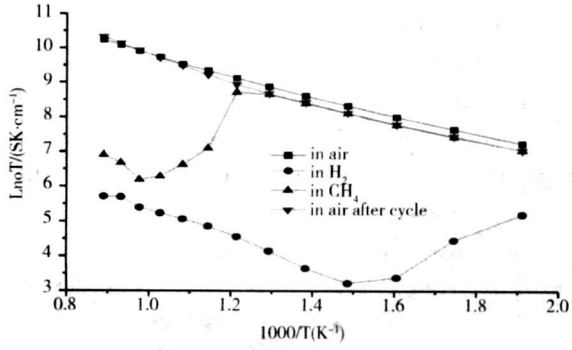

Fig. 4 Conductivity of LSCM7355 at different conditions

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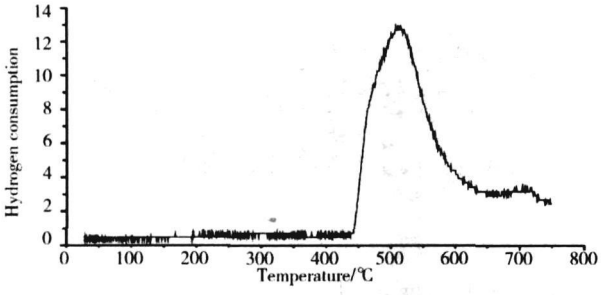

Fig. 5　H_2-TPR profile of LSCM7355 material

3　Conclusions

LSCM7355 material with single-phase perovskite is identified after sintering at 1 200 ℃ for 5 h and its molarratio of the elements agrees well with the designed value. LSCM7355 powder offer nanometer and micrometer size after sintering at 1 000 ℃ and 1 200 ℃ for 5 h, respectively. The total conductivity of LSCM7355 increases linearly with the temperature at air in the range from 250 ℃ to 850 ℃ and reaches 25 S/cm at 850 ℃, which becomes smaller in reducing atmosphere.

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甘氨酸 硝酸盐法合成 $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$阳极材料及性能研究

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摘　要：用甘氨酸 硝酸盐法合成了 $La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O_{3-\delta}$（LSCM7355）阳极材料。LSCM7355前驱体在 1 200 ℃下烧结 5 h后得到了单一钙钛矿型材料，材料中各元素摩尔比例与设计值吻合较好。1 000 ℃和 1 200 ℃烧结 5 h后，LSCM7355粉体分别为纳米和微米结构。在 250～850 ℃范围内，空气气氛下，LSCM7355的电导率符合小极化子绝热导电机理，其在 850 ℃时为 25 S/cm。LSCM7355材料在还原气氛下电导率比氧化气氛下低。

关键词：$La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$；阳极材料；甘氨酸 硝酸盐法；固体氧化物燃料电池；性能

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