Preparation and Characterization of $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ Anode Material for Solid Oxide Fuel Cell by Solid State Reaction

MA Xue-ju, MA Wen-hui, DAI Yong-nian, YANG Bin, LIU Rong-hui
(Faculty of Materials and Metallurgical Engineering; National Engineering Laboratory of Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, China)

Abstract: $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM) anode material of solid oxide fuel cell (SOFC) was prepared by solid state reaction method. The microstructure and properties of LSCM was tested via differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microcopy (SEM), AC impedance and four-probe direct current methods. Single-phase was prepared after being sintered at 1 250 ℃ and 1 350 ℃ for 15 h respectively. The electronic conductivity of LSCM enhanced with the temperature increasing and reached 29.2 S/cm at 850 ℃ in air. The AC impedance spectra show LSCM has good ionic conductivity.

Key words: solid oxide fuel cell; $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$; anode material; solid sate reaction method; conductivity
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Solid Oxide Fuel Cell (SOFC) has experienced in the last few years for its high electrical efficiency, low emissions and a multiple fuel choice. The anode material has to meet several stringent requirements including a good electronic conductivity and a high catalytic activity. It should also have a good match in coefficient of thermal expansion with adjacent components[1-2]. The perovskite structure oxide ABO_3 are being considered as anode materials. In $LaCrO_3$ materials, the conductivity is enhanced by a divalent ion such as Sr^{2+} substitution on A site, decreased polarization is attributed to the catalytic effect of Mn^{4+} substituted[3]. In this paper we investigated the characterization of Sr^{2+} and Mn^{4+}-substituted lanthanum chromo-manganite perovskites.

1 Experimental

1.1 Preparation of predecessor

$La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM7355) composition was synthesized via solid-state reaction. La_2O_3, $SrCO_3$, Cr_2O_3 and MnO_2 were mixed in light of the stoichiometry of LSCM7355. The pressed samples at loads of 150 MPa had the shape of pellets (Φ20 mm × 3 mm), and then sintered at different temperatures in air in a muffle furnace.

1.2 Characteristic

The water content and the mass loss of the precursor were measured by TG-DTA in Argon. The powders crystal structure was observed by XRD. The growth of crystal grain was observed with SEM. The conductivity was tested by AC impedance and four-probe direct current methods.

2 Results and discussion

2.1 TG-DTA analysis

The weight loss of the as-prepared powder LSCM7355 was observed by TG-DTA Fig. 1. An initial weight loss of about 4.3% below 420 ℃ corresponds of the decompose of $La(OH)_3$. Ma[4] think in the process $La(OH)_3$ spanning the Alkal-stype carbonate around 360 ℃ the Alkal-stype carbonate decomposed. The removing weight loss of 3.7% between 420 ~ 625 ℃. Another weight loss of 7.7% is between 625 ~ 1400 ℃, due to the separate out of crystal lattice oxygenic, at 977 ℃ has a big expend heat peak. After 997 ℃ there are nearly no loss of heat and molar, it is the process of perovskite forming.

2.2 X-ray diffraction (XRD) analysis

Fig. 2 illustrates the XRD patterns of LSCM7355 anode powder sintered at 1 250 ℃ and 1 350 ℃ in air for 15 h, which shows the single-phase perovskite was prepared after being sintered at both 1 250 ℃ and

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作者简介: 马学菊 (1981年生), 女, 硕士研究生; 通讯联系人: 马文会, E-mail: mwhui@kmust.edu.cn

1 350 ℃ in air for 15 h. Along with the increasing of temperature the diffraction peak of XRD patterns become more acuity. Illustrate high temperature made a more pure single-phase.

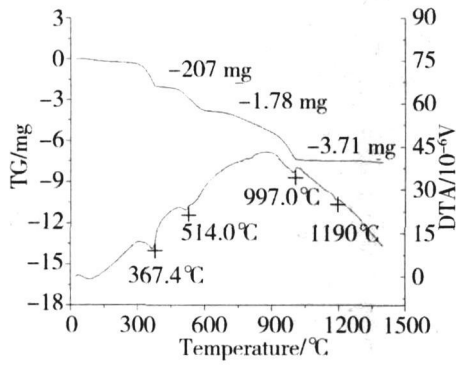

Fig. 1　TG-DTA curves for synthesizing LSCM 7355

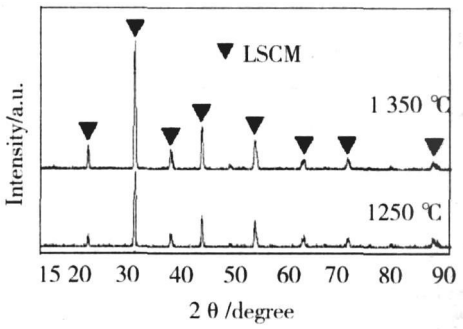

Fig. 2　XRD patterns of LSCM 7355 in air

2.3　SEM results for LSCM7355

Fig. 3 illustrates the SEM images of LSCM7355 anode sintered at 1 350 ℃ for 15 h. One can see the crystal looks slick and has no sharp refracting angle. But the size of crystal grain is non-uniform, it is difficult to get dense material. The low densification caused the decrease of conduction.

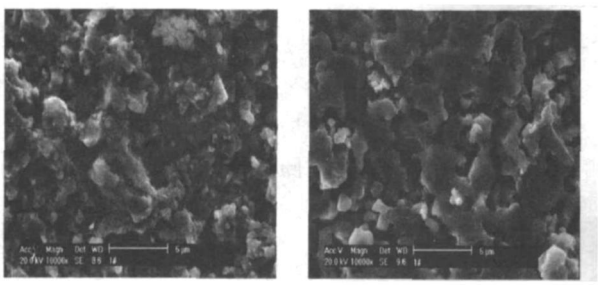

Fig. 3　SEM images of LSCM7355 sintered at 1350℃

2.4　The electricity of LSCM7355

Fig. 4 is the conductivities of LSCM7355 tested at 250 ~ 850 ℃ in different atmospheres with four-probe direct current method. In air below 650 ℃, the conductivity curve present linearity, the conductivity changes with temperature corresponding the small polaron mechanics[5]. After 650 ℃, large amounts of oxygen vacancy forming, the conductivity significantly enhanced for the increased oxygen partial pressure. The total conductivity measured at 850 ℃ in air is 29.2 S/cm. The figure also shows LSCM7355 have good reversible ability after deoxidized in the methane and hydrogen gas.

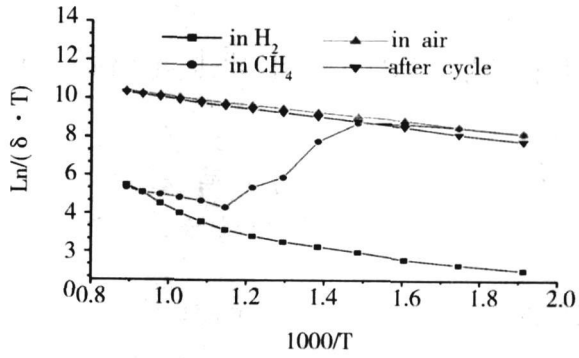

Fig. 4　Conductivity of LSCM7355 in different conditions

Fig. 5 shows the AC impedance pattern of LSCM7355 measured with the electrochemistry workstation in air. The AC impedance chart are formed with two half circularity. The AC impedance spectra show LSCM7355 has good ionic conductivity.

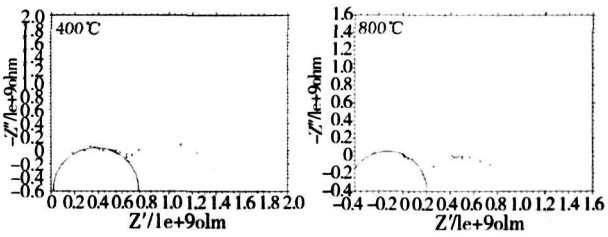

Fig. 5　The AC impedance of LSCM7355 at 400 ℃ and 800 ℃

3　Conclusions

(1) LSCM7355 anode material has the single-phase after being sintered both at 1 250 ℃ and 1 350 ℃ for 15 h respectively.

(2) The conductivity enhances followed the increasing of temperature, the conductivity measured at 850 ℃ in air is 29.2 S/cm.

(3) In the CH_4 and H_2 atmosphere, the conductivity is lower than that in air. But the reversible ability of LSCM7355 after deoxidized in CH_4 and H_2 is good.

References:

[1] MINH N Q. Ceramic fuel cells[J]. J Am Ceram Soc, 1993, 76(3): 563-588.

[2] METT, BY SAA. A direct-methane fuel cell with a ceria-based anode fuel cell[J]. Nature, 1999, (400): 649-951.

[3] SMP, PAÇ, ST. Electronic transport in the novel SOFC anode material $La_{1-x}Sr_xCr_{0.5}Mn_{0.5}O_{3-\delta}$[J]. Solid state ionic, 2006, (177): 2005-2008.

[4] MA W H. Study of Compositely Doped-Cathode Materials for Solid Oxide Fuel Cell (SOFC)[D]. Kunming: Kunming University of Science and Technology, 2001.

[5] TLW, NMM, ANDERSON H U, et al. Structure and electrical properties of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$[J]. Solid State Ionic, 1995, 76(3-4): 273-283.

固体氧化物燃料电池阳极材料 $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$的合成及性能研究

马学菊, 马文会, 戴永年, 杨 斌, 刘荣辉

(昆明理工大学 材料与冶金工程学院//真空冶金国家工程实验室, 云南 昆明 650093)

摘 要: 采用固相法制备 $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM) 固体氧化物燃料电池 (SOFC) 阳极材料, 用 TG-DTA和 X射线衍射分析仪分析了 LSCM材料中钙钛矿相的形成过程, 用 SEM, 直流四探针、交流阻抗等方法对合成材料的结构与性能进行研究。研究结果表明: 用固相法制备所得到的非晶产物分别在 1 250 ℃和 1 350 ℃下烧结 15 h都能得到单一的钙钛矿相, 对 LSCM样品电性能研究表明, 其电子电导率随温度的升高而增加, 在 850 ℃时空气状态下的电子电导率可达 29.2 S/cm; LSCM交流阻抗图是有由两个半圆组成的, 显示出良好的离子电导率.

关键词: 固体氧化物燃料电池; $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$; 阳极材料; 固相法; 电导率

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新型氧化添加剂 EGM影响柴油机性能和排放特性的研究

刘永启, 王延遐

(山东 理工大学 交通与车辆工程学院, 山东 淄博 255049)

摘 要: 提出了用含氧柴油添加剂 EGM降低柴油机碳烟排放的方法, 建立了超声波 EGM柴油在线混合装置, 在 4 JB1直喷柴油机上试验研究了含氧添加剂对发动机性能和排放特性的影响。结果表明, 在大负荷时随着混合燃料中的 EGM增加, 碳烟和 CO的排放显著降低; 对 NO_x的排放影响很小; 在小负荷时 HC的排放增加。

关键词: 乙二醇一乙酸酯; 含氧添加剂; 柴油机; 排放

中图分类号: TK421