Synthesis and Characterization of $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ for SOFC Cathode Materials

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Abstract: The solid oxide fuel cell technology offers substantial potential for clean and efficient power generation. $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ (LSFM) perovskites are potential materials used as cathode for intermediate temperature solid oxide fuel cell (ITSOFC). They (x = 0.1, 0.2, 0.3 and 0.4; y = 0.1, 0.2 and 0.3) were synthesized by a citrate method. The formed process of perovskite structure was analyzed using TG/DTA analysis. XRD showed the optimum formation of a single perovskite phase is 800℃. Electrical conductivity was measured by a four-probe DC method and $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ shows the highest conductivity. The oxygen nonstoichiometry was measured by Iodometric method. These perovskites display the oxygen deficient composition. LSFM, with increasing the number of Sr and Fe, increase the amount of oxygen vacancies. The synthesized $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ are chemically and thermally compatible well in XRD and SEM results. In conclusion, the LSFM can be considered as a promising cathode material for ITSOFC.

Key words: citrate method; LSFM perovskites; cathodes; electrical conductivity; compatibility
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1 Introduction

SOFC is a clean, efficient power generation technology[1]. The cathode is one component of a SOFC[2]. The properties[3-4] of the cathode play a significant role in determining the SOFC performance. Over the past decade, there has been an increasing interest in mixed ionic and electronic conducting perovskites. The present work aims at evaluating whether the LSFM is good or not for SOFC cathode materials with $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$ electrolyte[5].

2 Experimental

The $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ with x = 0.1, 0.2, 0.3 and 0.4 and y = 0.1, 0.2 and 0.3 perovskites were prepared by citrate method. The formation process of perovskite structure was analyzed using STA 449C TG/DTA. The phase purity of the compounds is evaluated with powder XRD using a Bruker D8 ADVANCE diffractometer. Electrical conductivity of sintered bars was measured as a function of temperature (250℃ ~ 850℃) under air atmosphere by a four-probe DC method. The oxygen nonstoichiometry was measured by Iodometric method. The chemical and thermal compatibility between LSFM and LSGM were studied using a XRD instrument and a XL30 TMP ESEM SEM instrument respectively.

3 Results and discussion

3.1 Preparation of LSFM

In Fig.1, no mass loss occurs above 600℃ suggesting that the formation of a LSFM perovskite is about 600℃. No additional diffraction peaks were found in the LSFM between 300℃ and 1200℃. After heating at 800℃, no significant change in tensity and the peak position in XRD pattern occurred (Fig.2). This is consistent with TG/DTA.

3.2 Electrical conductivity

As the amount of substitution of Sr and Fe for increases, the electrical conductivity also increases, as shown in Fig.3. $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ has the highest conductivity. It is about 26.0 S·cm⁻¹ at 850℃. The temperature dependence of electrical conductivity through the small polaron mechanism can be expressed by[6]:

$$\sigma = (A/kT^s)\exp(-Ea/kT)$$

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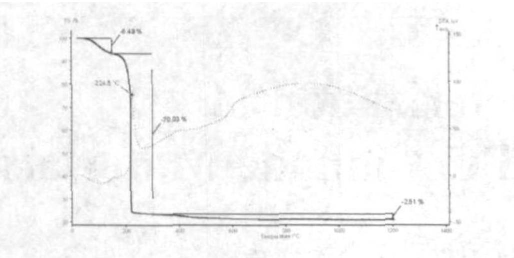

Fig. 1 DTA/TG curves of the LSFM precursor

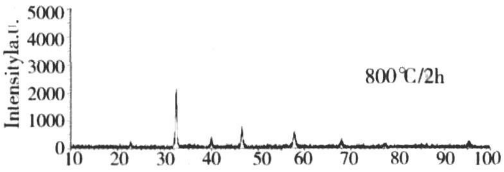

Fig. 2 XRD pattern of LSFM after sintering at 800℃

The plot of $\ln \sigma T$ versus $1/T$ for LSFM suggests that the adiabatic mechanism prevails over the measurement temperature range (Fig. 4).

3.3 Oxygen nonstoichiometry

These perovskites display the oxygen deficient composition. LSFM, with increasing the number of Sr and Fe, increase the amount of oxygen vacancies. $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ has the highest oxygen nonstoichiometry value 0.23.

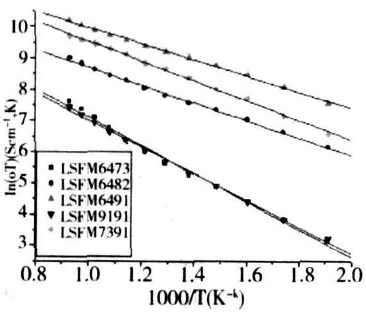

Fig. 3 $1/T$ dependence of $\ln \sigma t$ for $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ sample

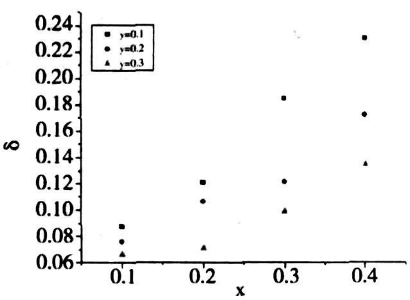

Fig. 4 The oxygen nonstoichiometry δ for $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$

3.4 Chemical compatibility of LSFM and LSGM

The compositions of powders of LSFM and LSGM after sintering at 1250℃ exhibit pure perovskite as shown in Fig. 5. This indicates that the composite is stable in air at high temperature.

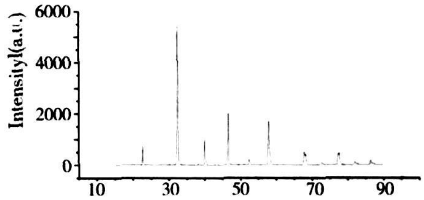

Fig. 5 XRD patterns of LSFM and LSGM sintered at 1250℃

3.5 Thermal compatibility

The prepared LSFM cathode film is in good contact to the LSGM electrolyte at 1250℃ (Fig. 6). The LSFM cathode film is porous (Fig. 7), which is good for permeation and reduction of oxygen.

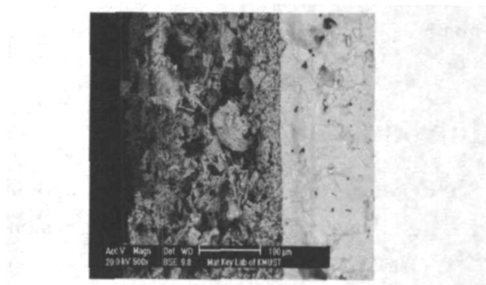

Fig. 6 SEM images of LSGM-based LSFM cathode film

Fig. 7 SEM image of LSFM cathode film

4 Conclusions

(1) The optimum heat treatment temperature is 800 ℃;

(2) The electrical conductivity enhances as the amount of Fe and Sr increases. $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ has the highest conductivity about 26.0 S·cm^{-1} at 850℃. The mechanism of electrical conductivity is adiabatic mechanism;

(3) LSFM, with increasing the number of Sr and Fe, increase the amount of oxygen vacancies. $La_{0.6}$

$Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ has the highest oxygen nonstoichiometry value of 0.23;

(4) The composition of powders of LSFM and LSGM is stable at high temperature;

(5) The LSFM painted on the LSGM electrolyte is porous.

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固体氧化物燃料电池阴极材料 $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$的合成与性能表征

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摘 要：固体氧化物燃料电池技术提供清洁、高效的发电方式。$La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ (LSFM) 钙钛矿作为中温固体氧化物阴极材料受到人们的关注。本文用柠檬酸盐法合成了 $La_{1-x}Sr_xFe_{1-y}Mn_yO_{3-\delta}$ ($x=0.1, 0.2, 0.3, 0.4$; $y=0.1, 0.2, 0.3$) 钙钛矿阴极材料。使用同步热分析仪 (TG/DTA) 研究了钙钛矿结构的形成历程。XRD衍射结果证明单一钙钛矿相的最佳形成温度是 800℃。采用直流四探针法测试了样品的电导率，其中 $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$显示了最高值。用碘量法测量了 LSFM中的非化学计量氧值。随着 Sr与 Fe的增加，非化学计量氧值增大。通过 XRD与 SEM分析，$La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_{3-\delta}$与 $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$之间显示出较好的化学和热相容性。结果表明 LSFM有望作为中温固体氧化物燃料电池的阴极材料。

关键词：柠檬酸盐法；LSFM钙钛矿；阴极；电导率；相容性

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