Preparation of $Ce_{0.8}Gd_{0.2}O_{1.85}$ Anode Materials by Glicine Nitrate Method

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Abstract: The $Ce_{0.8}Gd_{0.2}O_{1.85}$ (GDC82) anode materials were prepared by glycine-nitrate method (GNM). The properties of GDC82 materials were analysized by using X-ray diffraction (XRD), direct current four point probes (DC-FPP) and temperature process reduce (TPR) techniques methods. The total conductivity becomes bigger when the atmosphere changes from air to hydrogen, which greatly increases with the increasing of the temperature and reaches to the maximum value 0.4 S/cm at 850℃. GDC82 and $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM) anode materials have good chemical compatibility. The catalytic result shows that GDC82 as anode materials has the excellent catalytic property for hydrogen and methane.

Key words: $Ce_{0.8}Gd_{0.2}O_{1.85}$; glycine-nitrate; conductivity property; catalytic property
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Anode material is one of the key components of solid oxide fuel cell (SOFC). The precious metals such as platinum and silver were used as anode material at first, but which have few applications now for some reasons such as high price and evaporation of silver[1-3]. Now, the nickel and electrolyte composite material is often used as anode, many problems[1,4] such as the serious agglomeration of anode, carbon deposition at anode when using fuel containing carbon and the poor tolerance of sulfur still exist. Furthermore, the total conductivity of anode decreases for the relatively low conductivity of electrolyte (such as YSZ and LSGM) materials, and the catalytic property of composite anode becomes poor for the above electrolyte materials. The novel anode materials must have high mixed (ionic and electronic) conductivity and excellent catalytic property at the low and intermediate (600 ~ 800℃) temperatures.

The CeO_2-based materials as electrolyte of the low temperature SOFC were studied by many researchers[5-6]. Oxygen vacancies emerge when CeO_2 is doped by Sm^{3+} and Gd^{3+} and the conductivity greatly increases. The CeO_2-based materials have excellent catalytic properties and often applied in the water-vapor reforming and direct degradation of hydrocarbon industry. So, the CeO_2-based anode materials have a good promising prospect in SOFC using hydrocarbon as fuel. In this paper, the $Ce_{0.8}Gd_{0.2}O_{1.85}$ (GDC82) materials were synthesized by glycine-nitrate process (GNP). It was studied the conductivity property, and catalytic property and the chemical compatibility of GDC82 materials with LSGM electrolyte materials at different conditions, and all these tests make it interesting for GDC to be studied as possible anode materials for SOFC.

1 Experimental

The $Ce(NO_3)_4 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$ with a molar ratio 8:2 were resolved into distilled water. Gel was obtained after the solution was heated and strenuous combustion continued at about 250℃. The crystal structure of the GDC82 powder was examined by X-ray diffraction (XRD). The chemical compatibility between LSGM and GDC82 was researched after being mixed with the weight proportion of 1:1 with using XRD. Temperature process reducing (TPR) experiments of GDC82 was performed with pure hydrogen carrier gas.

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2 Results and discussion

2.1 Phase characterization and conductivity property of GDC82

Fig.1 illustrates the XRD patterns of GDC82 powder sintered at 900℃ for 4 h. Fig.2 illustrates the total conductivity of GDC82 at air and pure hydrogen.

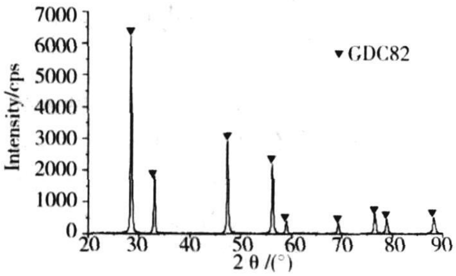

Fig.1 XRD pattern of the precursors of GDC82 sintered at 900℃ for 4 h

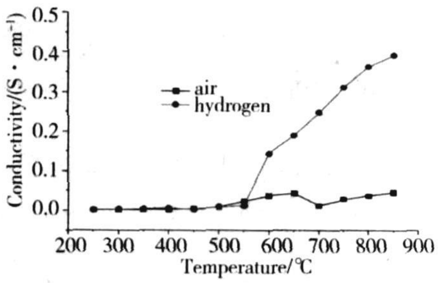

Fig.2 Conductivity of GDC82 material at different temperatures and in different atmospheres

Fig.1 in accordance with shows that pure fluorite phase exists after the sintered predecessor, which indicates that the Gd^{3+} replaced Ce^{4+} well. According to Fig.1, the diffraction peaks of GDC82 are very sharp, displaying that the crystal crystalline grains grow well.

According to Fig.2, the oxygen vacancies exist when the Ce^{4+} is replaced by Ga^{3+} in air, and the material is in accordance with ionic type conductor and has low conductivity. The ionic conductivity changes little between 250 and 850 ℃, and which reaches to be the maximum value 0.4 S/cm at 850℃. From the relative thermodynamic, it can conclude CeO_2 can be reduced to be $CeO_{1.83}$ and $CeO_{1.73}$ at low temperatures, and more and more Ce^{4+} change to be Ce^{3+} with temperature. So, the electrical type changes from ionic to ionic-electronic mixed one when the experimental atmosphere changes from air to hydrogen, and the total conductivity increases.

2.2 Chemical compatibility and catalytic property between GDC82 and LSGM

Fig.3 illustrates the XRD patterns of the mixed powders of LSGM and GDC82 sintered at 1200 ℃ in air for 15 h. Fig.4 shows the products and their contents of the catalytic reactions of CeO_2-methane and GDC82-methane at 850 ℃.

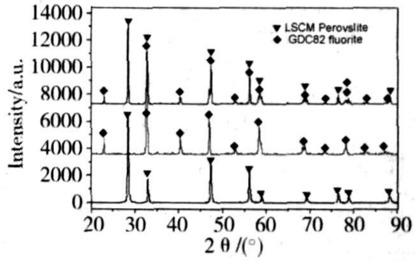

Fig.3 XRD patterns of LSCM (▼), GDC82 (◆) and mixture of them sintered at 1200℃ for 15 h

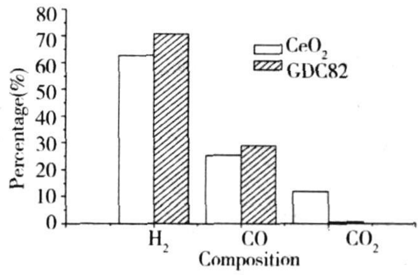

Fig.4 Products of the catalytic reactions of CH_4 by CeO_2 and GDC82 at 850℃

According to Fig.3, it does not exist the impurities during the sintering process at 1200℃ high temperature. It shows that chemical reaction does not happen between GDC82 and LSCM, and it also indicates that the chemical compatibility between GDC82 and LSGM is good, these two materials are suitable for the fabrication of LSGM-based GDC82 anode film.

According to Fig.4, the selectivity of GDC82 to H_2 and CO are higher than that of CeO_2, the combined gas with H_2 and CO occupy 99% in the whole GDC82 system, and the produced content of CO_2 after being catalytized by GDC82 is lower that that of CeO_2, it is helpful for the next electro-chemical oxidation, and this can improve the generating efficiency.

3 Conclusions

(1) The results showed that pure fluorite phase can be obtained after the sintered process according to XRD pattern, the diffraction peaks of GDC82 are very sharp, displaying that the crystal crystalline grains grow well.

(2) The conductivity of GDC82 in the atmosphere is not high, when the atmosphere is changed into hydrogen, the conductivity of GDC82 increased as a whole, and it also appeared the increasing trend with the increasing the temperature. The whole conductivity

of GDC82 is 0.4 S/cm at 850 ℃. The chemical compatibility between GDC82 and LSGM is good and these two materials are suitable for the fabrication of LSGM-based GDC82 anode film.

(3) The products of methane being catalytized by GDC82 is almost H_2 and CO, it is helpful for the next electro-chemical oxidation, and this can improve the generating efficiency.

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甘氨酸—硝酸盐法制备 $Ce_{0.8}Gd_{0.2}O_{1.85}$阳极材料的研究

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摘 要：采用甘氨酸—硝酸盐法制备了 $Ce_{0.8}Gd_{0.2}O_{1.85}$ (GDC82) 阳极材料。用 XRD, DC-FP, TPR等技术对材料的性能进行表征。GDC82在 H_2气氛下的总电导率整体增加，且随温度的升高而迅速增加，在 850℃达到 0.4 S/cm, GDC82与 $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ (LSCM) 阳极材料化学相容性较好，且对氢气和甲烷具有较好的催化氧化效果。

关键词：$Ce_{0.8}Gd_{0.2}O_{1.85}$；甘氨酸-硝酸盐；导电性能；催化性能

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